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Chemical Calculations

BY

R. HARMAN ASHLEY, PH. D.

ASSISTANT PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF MAINE

ILLUSTRATED

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PREFACE

In putting forth this small work, the author has intended to write a textbook on Chemical Calculations following more closely than other books at present on the market, the needs of the student who will later find occupation in chemical laboratory work. For this reason, constant reference will be made to Chemists' Handbooks, the best of which, in the author's opinion, is "Van Nostrand's Chemical Annual for 1913," edited by Prof. J. C. Olsen. Constant reference will be made to this work by means of footnotes, with the intention of leading the student to the most convenient source of tabulated data, and to explain the method of utilizing the same. The purchase of the "Annual" will not be necessary, much as it may be desirable, in following the explanations or solving the problems.

The problems are numerous and of varying degrees of difficulty; the instructor is the best judge of the type of problem to assign a class or individual. Those of the more difficult sort may be given the more advanced student, thus holding the class together. Many of the problems conform to the type usually found in works of this nature and in the selection of these, most of the books on this subject have been consulted. Some of the types are new to works of this kind; their inclusion is made in the hope of making the book more practical.

The method of solving the problems is treated in the text, and in the earlier chapters typical problems are solved at the end of the reading matter just before the problems are stated. The answer or answers have been

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attached to each problem rather than given in a list in the appendix, with the belief that it is more convenient for student and instructor. It may be urged that the inclusion of the answer with the problem may be a temptation offered the student to work for this answer. However, a student who will do this, will always take the trouble of looking up the answer, even if it is at the end of the book.

Some of the topics are discussed from two or more methods of approach in the belief that one of the methods may appeal to a student and be more easily comprehended by him than the others. If some of the topics are treated in too elementary or extended a fashion to suit some, it must be remembered that this subject is not simple to all students. The author does not anticipate adverse criticism on the score of the work being too elementary when taken as a whole. The treatment of ratios may be so full as to be tedious. This is for the reason that it is wished to lead the student away from proportions as generally expressed, *i.e.*, $x : y = a : b$, but to have him at once set down his mathematical expression in a form for immediate solution. The algebraic method has been extensively employed and the treatment of indirect analysis and the calculation of indirect factors have been given considerable space, an amount of space not measured by the importance of indirect analysis, but rather by the importance of the methods of chemical and algebraic reasoning. Many problems have been solved in steps, after which it is shown how the same problem may be solved by one expression. The problems are more numerous than will be solved by one class, if small; two or more problems of the same nature are included so that in a large class there will be enough to go around. Furthermore, a large number of problems will give the

instructor more choice, and there is less likelihood of their being solved by one class and handed on to the next in the nature of heirlooms.

In the calculation of the problems, the use of logarithms is strongly recommended; as also is the slide rule. The latter is to be especially recommended, as the time allotted the subject may be devoted to theory, relegating the mechanical solution of the problems to a subordinate place. With the use of this device the subject may be thoroughly treated in half the usual time.

The problems have been checked and rechecked, but notwithstanding this, errors will undoubtedly creep in. The author will appreciate having his attention called to such. As five- and, in a few instances, six-place logarithms have been used, answers are often stated to a number of significant figures not justified by the number of significant figures in the data given. It was thought best to carry out the answer, as this involved no extra work and is valuable in inculcating accuracy.

The author wishes to express his appreciation to Mr. Harry R. Lee, Superintendent, of the Virginia Electrolytic Company for checking problems, reading the manuscript and giving much criticism and advice; to Mr. G. C. Merrill, formerly of the College of Montana, for the checking of a large number of problems. Professors Ralph H. McKee and Charles W. Easley of the University of Maine have been generous with help and advice, as have many others of the author's colleagues. An expression of thanks is due Mr. Charles F. Guhlmann of the General Chemical Company for reading the chapter on mixed acids and offering very helpful advice for this section.

R. H. A.

UNIVERSITY OF MAINE,
ORONO, MAINE,
Jan. 30, 1915.

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CHEMICAL CALCULATIONS

CHAPTER I

RATIOS

CHEMICAL calculations are based on the two following laws:

Law of the Conservation of Mass. — In any system undergoing change, chemical or otherwise, no change in the mass of the system has ever been observed.

Law of Constancy of Composition. — The masses of the elements taking part in a given chemical change always exhibit a definite and invariable ratio to each other.

The Decomposition of Mercuric Oxide. — Let it be required to find the number of grams of oxygen which will be liberated by the decomposition of 1.7000 g. of mercuric oxide. The decomposition is represented by the equation:

$$2\,HgO = 2\,Hg + O_2$$

parts by weight, 2 (216.6) 2 (200.6) 2 (16)

In the atomic weight tables,[1] 200.6 is given as the atomic weight of mercury and 16.00 as that of oxygen. The symbol of mercuric oxide, HgO, shows that one molecule of mercuric oxide contains one atomic weight of mercury

[1] The atomic weights are revised annually by an international committee. See "Van Nostrand's Chemical Annual," p. 1, third issue, 1913. Frequent reference will be made to this book, where the title will be abbreviated to Chem. Ann., always referring to the edition of 1913.

and one atomic weight of oxygen, consequently the sum of these atomic weights (200.6 + 16.00), 216.60, represents the molecular weight of mercuric oxide.[1] Single atoms and molecules are so small that they cannot be dealt with as such, but aggregations of atoms or molecules may be taken in the ratio of their atomic or molecular weights, in which case an equal number of atoms are dealt with. Numbers representing molecular or atomic weights are relative only, being based upon a convenient standard, for example, the weight of an atom of oxygen, the atomic weight of which is arbitrarily fixed at 16.00. In a complete reaction, when all the initial substances are adjusted in the ratio of the molecular or atomic weights, all the initial substances disappear and the products stand in relation to each other in the ratio of their molecular or atomic weights and nothing remains over.

Ratios Involved in the Decomposition of Mercuric Oxide. — Returning to the problem, the ratio of oxygen to mercuric oxide is 2 (16) parts by weight of oxygen to 2 (216.6) parts by weight of mercuric oxide, or $\frac{2\,(16)}{2\,(216.6)}$. This is the fixed and invariable ratio which always holds between these two substances in this particular reaction. In other words, 2 (16) parts by weight of oxygen are evolved by the decomposition of 2 (216.6) parts by weight of mercuric oxide. Then, if 2 (216.6) parts by weight of mercuric oxide yield 2 (16) parts by weight of oxygen, one part by weight of oxygen is given by $\frac{2\,(16)}{2\,(216.6)}$ parts by weight of

[1] Tabulations of molecular weights are to be found in chemist's handbooks. In such a simple case as this, no time would be saved by so doing, but in many cases such tabulations are useful and much time saved and liability to error reduced. See Chem. Ann., pp. 39–47; 100–336.

mercuric oxide, and as the unit of weight under consideration is the gram, the problem is solved by the expression:

$\frac{2\,(16)}{2\,(216.6)} \times 1.7000 = 0.1256$ g. of oxygen, yielded by 1.7000 g. mercuric oxide.

Again, employing the same equation, how much mercury will be obtained by the decomposition of 1.7000 g. of mercuric oxide? The quantity of mercury is now sought; consequently the ratio of mercury to mercuric oxide being $\frac{2\,(200.6)}{2\,(216.6)}$, and reasoning precisely as in the previous problem, the expression becomes:

$\frac{2\,(200.6)}{2\,(216.6)} \times 1.7000 = 1.5744$ g. of mercury, yield from 1.7000 g. mercuric oxide.

In all, this reaction yields the following ratios:

(*a*)[1] Oxygen to mercuric oxide, $\frac{2\,(16)}{2\,(216.6)}$.

(*b*) Oxygen to mercury, $\frac{2\,(16)}{2\,(200.6)}$.

(*c*) Mercury to mercuric oxide, $\frac{2\,(200.6)}{2\,(216.6)}$.

[1] It is evident that $\frac{2\,(16)}{2\,(216.6)}$, etc., is equivalent to $\frac{16}{216.6}$; but the equation as written is more accurate, chemically speaking, than the simpler equation, HgO = Hg + O, in which the oxygen is represented as in the atomic state, a condition fulfilled only at the instant of decomposition. It is necessary for the student to bear this in mind, as in gas equations involving volumes it is a matter of importance. For calculations involving weights only, such an equation serves the purpose, but in the calculation it is a simple matter to write the correct equation, and in solving to cancel; *i.e.*, $\frac{\not{2}\,(16)}{\not{2}\,(216.6)} = \frac{16}{216.6}$.

(a) Mercury to oxygen. $\frac{2 \times 200.6}{2 \times 16}$.

(b) Mercuric oxide to oxygen. $\frac{2 \times 216.6}{2 \times 16}$.

(c) Mercuric oxide to mercury. $\frac{2 \times 216.6}{2 \times 200.6}$.

If x represents the units of weight in any system:

(a) $\frac{2 \times 16}{2 \times 216.6} x$ = weight of O_2 produced by x units of HgO.

(b) $\frac{2 \times 16}{2 \times 200.6} x$ = weight of O_2 equivalent to x units of Hg.

(c) $\frac{2 \times 200.6}{2 \times 216.6} x$ = weight of Hg produced by x units HgO.

(d) $\frac{2 \times 200.6}{2 \times 16} x$ = weight of Hg equivalent to x units of O_2.

(e) $\frac{2 \times 216.6}{2 \times 16} x$ = weight of HgO produced by x units of O_2.

(f) $\frac{2 \times 216.6}{2 \times 200.6} x$ = weight of HgO produced by x units of Hg.

These six ratios are applied in problems typified by the following:

(a) How many grams of oxygen will be liberated by the decomposition of 5.000 g. of mercuric oxide?

$$Ans. \quad \frac{2 \times 16}{2 \times 216.6} \times 5.000 = 0.2216 \text{ g.}$$

(b) How many grams of oxygen are associated with 5.000 g. of mercury in mercuric oxide?

$$Ans. \quad \frac{2 \times 16}{2 \times 200.6} \times 5.000 = 0.2393 \text{ g.}$$

(*c*)″ How many grams of mercury are produced by the decomposition of 3.000 g. of mercuric oxide?

$$Ans. \quad \frac{2\,(200.6)}{2\,(216.6)} \times 3.000 = 2.7784 \text{ g.}$$

(*d*)″ How many grams of mercury are associated with 3.000 g. of oxygen in mercuric oxide?

$$Ans. \quad \frac{2\,(200.6)}{2\,(16)} \times 3.000 = 37.613 \text{ g.}$$

(*e*)″ How many grams of mercuric oxide must be decomposed to obtain 3.000 g. of oxygen?

$$Ans. \quad \frac{2\,(216.6)}{2\,(16)} \times 3.000 = 40.613 \text{ g.}$$

(*f*)″ How many grams of mercuric oxide must be decomposed to obtain 3.000 g. of mercury?

$$Ans. \quad \frac{2\,(216.6)}{2\,(200.6)} \times 3.000 = 3.239 \text{ g.}$$

Metathesis between Barium Chloride and Sodium Sulphate. — Again take the equation:

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2\,NaCl.$$

The molecular weights being the sum of the atomic weights, are:

$BaCl_2$		Na_2SO_4	
Ba	= 137.37	Na_2 = 2 (23.00)	= 46.00
2 Cl = 2 (35.46)	= 70.92	S	= 32.07
	208.29	4 O = 4 (16.00)	= 64.00
			142.07

$BaSO_4$		2 NaCl	
Ba	= 137.37	Na	= 23.00
S	= 32.07	Cl	= 35.46
4 O = 4 (16.00)	= 64.00		2 (58.46)
	233.44		

As before the ratios are:

(*a*) Barium chloride to sodium sulphate: $\frac{208.29}{142.07}$.

(*b*) Barium chloride to barium sulphate: $\frac{208.29}{233.44}$.

(*c*) Barium chloride to sodium chloride: $\frac{208.29}{2\,(58.46)}$.

(*d*) Sodium sulphate to barium chloride: $\frac{142.07}{208.29}$.

(*e*) Sodium sulphate to barium sulphate: $\frac{142.07}{233.44}$.

(*f*) Sodium sulphate to sodium chloride: $\frac{142.07}{2\,(58.46)}$.

(*g*) Barium sulphate to barium chloride: $\frac{233.44}{208.29}$.

(*h*) Barium sulphate to sodium sulphate: $\frac{233.44}{142.07}$.

(*i*) Barium sulphate to sodium chloride: $\frac{233.44}{2\,(58.46)}$.

(*j*) Sodium chloride to barium chloride: $\frac{2\,(58.46)}{208.29}$.

(*k*) Sodium chloride to sodium sulphate: $\frac{2\,(58.46)}{142.07}$.

(*l*) Sodium chloride to barium sulphate: $\frac{2\,(58.46)}{233.44}$.

These twelve ratios cover all cases which will arise from this reaction. In the typical examples given below, these ratios are employed in solving problems.

(*a*)′ How many grams of barium chloride will be required to react with (are equivalent to) 5.0000 g. of sodium sulphate?

Ans. $\frac{208.29}{142.07} \times 5.0000 = 7.3305$ g.

(*b*)′ How many grams of barium chloride are required for the precipitation of 5.0000 g. of barium sulphate?

$$Ans. \quad \frac{208.29}{233.44} \times 5.0000 = 4.4613 \text{ g.}$$

(*c*)′ Required the number of grams of barium chloride equivalent to 5.0000 g. of sodium chloride.

$$Ans. \quad \frac{208.29}{2\,(58.46)} \times 5.0000 = 8.9074 \text{ g.}$$

(*d*)′ How many grams of sodium sulphate are necessary for the precipitation of the barium of 5.0000 g. of barium chloride?

$$Ans. \quad \frac{142.07}{208.29} \times 5.0000 = 3.4104 \text{ g.}$$

(*e*)′ How many grams of sodium sulphate have been added to barium chloride if 5.0000 g. of barium sulphate are precipitated?

$$Ans. \quad \frac{142.07}{233.44} \times 5.0000 = 3.0430 \text{ g.}$$

(*f*)′ How many grams of sodium sulphate are equivalent to 5.0000 g. of sodium chloride?

$$Ans. \quad \frac{142.07}{2\,(58.46)} \times 5.0000 = 6.0755 \text{ g.}$$

(*g*)′ How many grams of barium sulphate are precipitated by 5.0000 g. of barium chloride?

$$Ans. \quad \frac{233.44}{208.29} \times 5.0000 = 5.6037 \text{ g.}$$

(*h*)′ How many grams of barium sulphate are precipitated by 5.0000 g. of sodium sulphate?

$$Ans. \quad \frac{233.44}{142.07} \times 5.0000 = 8.2157 \text{ g.}$$

(*i*)′ How many grams of barium sulphate are equivalent to 5.0000 g. of sodium chloride?

$$Ans. \quad \frac{233.44}{2\,(58.46)} \times 5.0000 = 9.9829 \text{ g.}$$

(*j*)′ How many grams of sodium chloride are formed when 5.0000 g. of barium chloride are added to a solution containing sodium sulphate?

$$Ans. \quad \frac{2\,(58.46)}{208.29} \times 5.0000 = 2.8067 \text{ g.}$$

(*k*)′ How many grams of sodium chloride are equivalent to 5.0000 g. of sodium sulphate?

$$Ans. \quad \frac{2\,(58.46)}{142.07} \times 5.0000 = 4.1149 \text{ g.}$$

(*l*)′ If 5.0000 g. of barium sulphate are precipitated, how many grams of sodium chloride are formed?

$$Ans. \quad \frac{2\,(58.46)}{233.44} \times 5.0000 = 2.5043 \text{ g.}^{1}$$

[1] These examples are typical of the commonest and simplest chemical calculations. It is to be noted that there are three terms, of which two are expressed in similar units, the third being dissimilar. In these examples there are two terms expressing atomic weights and one term in grams. To solve a problem of this type: MAKE A FRACTION OF THE TWO TERMS IN SIMILAR UNITS, PLACING THAT TERM REPRESENTING THE MAGNITUDE SOUGHT OVER THE LINE (MAKING IT THE NUMERATOR), THE OTHER TERM OF THE SAME KIND OF UNIT UNDER THE LINE (MAKING IT THE DENOMINATOR), MULTIPLY BY THE TERM OF THE DISSIMILAR UNIT.

This rule of constructing ratios is, as stated, empirical, but a little reflection will show its validity. It is given in this form in the belief that it is more easily grasped and that a little practice will result in making application of it almost mechanical. It must be borne in mind that it is applicable only when an increase in one term produces a corresponding increase in the other; in other words, in those cases only in which the two units going to make up the fraction vary *directly*. The great majority of chemical problem

Factors. — The fractions composed of the terms of similar units are constant for the same equation and when frequently employed it is advantageous to solve the ratio once for all. The values thus obtained are called factors.[1] In the reaction between barium chloride and sodium sulphate, the fractions formed by the molecular weights yield the following constants:

(*a*)" $\frac{BaCl_2}{Na_2SO_4} = \frac{208.29}{142.07} = 1.4661$: factor of $BaCl_2$ to Na_2SO_4.

(*b*)" $\frac{BaCl_2}{BaSO_4} = \frac{208.29}{233.44} = 0.8923$: factor of $BaCl_2$ to $BaSO_4$.

(*c*)" $\frac{BaCl_2}{2\,NaCl} = \frac{208.29}{2\,(58.46)} = 1.7815$: factor of $BaCl_2$ to NaCl.

(*d*)" $\frac{Na_2SO_4}{BaCl_2} = \frac{142.07}{208.29} = 0.6821$: factor of Na_2SO_4 to $BaCl_2$.

(*e*)" $\frac{Na_2SO_4}{BaSO_4} = \frac{142.07}{233.44} = 0.6086$: factor of Na_2SO_4 to $BaSO_4$.

(*f*)" $\frac{Na_2SO_4}{2\,NaCl} = \frac{142.07}{2(58.46)} = 1.2151$: factor of Na_2SO_4 to NaCl.

(*g*)" $\frac{BaSO_4}{BaCl_2} = \frac{233.44}{208.29} = 1.1207$: factor of $BaSO_4$ to $BaCl_2$.

(*h*)" $\frac{BaSO_4}{Na_2SO_4} = \frac{233.44}{142.07} = 1.6431$: factor of $BaSO_4$ to Na_2SO_4.

come under this head, the chief exceptions being in gas calculations, as for instance Boyle's law, which states that the volume of a gas varies *inversely* with the pressure. In such cases the rule is reversed so far as the composition of the fraction is concerned. This is treated in another place.

[1] See Chem. Ann., pp. 10–36.

[2] When chemical symbols are written in this manner, the fraction is considered as made up of the terms corresponding to the molecular weight of the symbol, $\frac{BaCl_2}{Na_2SO_4}$ representing the fraction $\frac{208.29}{142.07}$.

Factors as given in chemists' handbooks are usually tabulated in four columns: Given, Sought, Factor and Logarithm of the factor. In problem (*b*)″ barium sulphate is given; barium chloride is sought and the factor is 0.8923. In problem (*g*)″ these conditions are reversed; barium chloride is given and barium sulphate is sought; consequently the operation is reversed.[1]

Percentage Composition of Chemical Compounds. — The law of constancy of composition, stating that every well-defined chemical compound always consists of the same elements united in invariable proportion by weight, furnishes a means of calculating the ratio composition of any compound and consequently the weight of any element or group of elements contained in any weight of that compound. The compound $MgSO_4 \cdot 7\ H_2O$ is composed of

$$\frac{Mg}{MgSO_4 \cdot 7\ H_2O} = \frac{24.32}{246.50} = 0.0987 \text{ parts of}$$

magnesium, per unit weight $MgSO_4 \cdot 7\ H_2O$,

$$\frac{S}{MgSO_4 \cdot 7\ H_2O} = \frac{32.07}{246.50} = 0.1301 \text{ parts of}$$

sulphur per unit weight $MgSO_4 \cdot 7\ H_2O$.

$$\frac{11\ O}{MgSO_4 \cdot 7\ H_2O} = \frac{11\ (16)}{246.50} = 0.7140 \text{ parts of}$$

oxygen per unit weight $MgSO_4 \cdot 7\ H_2O$,

[1] See Chem. Ann., p. 13. In this tabulation, both factors are given, one being the reciprocal of the other. In the problem (*b*), barium chloride is "required," while barium sulphate is "found." An inspection of the arrangement of the tables will show when the column headed "*a*" is to be used, as the line giving the conditions of "required" and "found" are given on the line marked "*A*." The factor (*g*)″ is found in column "*B*" as the line marked "*B*" fulfills the conditions of the problem.

$$\frac{14\ H}{MgSO_4 \cdot 7\ H_2O} = \frac{14\ (1.008)}{246.50} = \frac{0.0572}{1.0000} \text{ parts of}$$

hydrogen per unit weight $MgSO_4 \cdot 7\ H_2O$.

Or, if magnesium sulphate is regarded as made up of the radicals, $MgO \cdot SO_3 \cdot 7\ H_2O$, then

$$\frac{MgO}{MgSO_4 \cdot 7\ H_2O} = \frac{40.32}{246.50} = 0.1636 \text{ parts of}$$

magnesium oxide.

$$\frac{SO_3}{MgSO_4 \cdot 7\ H_2O} = \frac{80.07}{246.50} = 0.3248 \text{ parts of}$$

sulphur trioxide,

$$\frac{7\ H_2O}{MgSO_4 \cdot 7\ H_2O} = \frac{7\ (18.016)}{246.50} = \frac{0.5116}{1.0000} \text{ parts of water.}$$

Equivalents. — If a compound contains the elements of a radical, even though it be impracticable actually to convert the compound into the desired radical, yet the amount of the radical which might theoretically be derived if the conversion were possible is readily calculated, though the equations may be lacking. Thus: what is the arsenic trioxide equivalent of potassium arsenite? Representing the equivalence by the sign ≡,

$$K_3AsO_3 \rightarrow As_2O_3.$$

But arsenic trioxide contains two atoms of arsenic in the molecule while potassium arsenite contains only one atom of arsenic; hence two molecules of potassium arsenite must be taken,

$$2\ K_3AsO_3 \equiv As_2O_3$$

and the factor is

$$\frac{As_2O_3}{2\ K_3AsO_3} = \frac{197.92}{2\ (240.22)} = 0.4112.$$

Successive Reactions. — When a compound is converted into some other substance by successive steps, and the amount of one of the initial compounds, needed to furnish a certain amount of a final product, is required, it is unnecessary to calculate the intermediary products. For example, the Solvay process for the manufacture of sodium carbonate depends upon the equations:

$$NH_3 + H_2O + CO_2 = NH_4HCO_3,$$
$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl,$$
$$2\,NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

It is desired to know the amount of ammonia involved in the production of one ton of sodium carbonate. It is needless to calculate the amount of acid ammonium carbonate and of acid sodium carbonate; it is necessary only to notice that one molecule of ammonia yields one molecule of acid ammonium carbonate which in turn yields one molecule of acid carbonate, while it requires *two* molecules of acid sodium carbonate to yield one molecule of sodium carbonate. The equations must then be modified to

$$2\,NH_3 + 2\,H_2O + 2\,CO_2 = 2\,NH_4HCO_3,$$
$$2\,NaCl + 2\,NH_4HCO_3 = 2\,NaHCO_3 + 2\,NH_4Cl,$$
$$2\,NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The sodium carbonate depends upon acid sodium carbonate for its production, the weight of which, requisite to produce one ton of sodium carbonate, being

$$\frac{2\,NaHCO_3}{Na_2CO_3} \times 1 = X \text{ tons of } NaHCO_3; \qquad (1)$$

and X tons of acid sodium carbonate require

$$\frac{2\,NH_4HCO_3}{2\,NaHCO_3} \times X = Y \text{ tons of } NH_4HCO_3; \qquad (2)$$

and the production of Y tons of ammonium acid carbonate call for

$$\frac{2\,NH_3}{2\,NH_4HCO_3} \times Y = Z \text{ tons of ammonia.} \qquad (3)$$

Substituting in (2) the value of X found in (1), the result is

$$\frac{2\,NH_4HCO_3}{2\,NaHCO_3} \times \frac{2\,NaHCO_3}{Na_2CO_3} \times 1 = Y;$$

and substituting in (3) this value of Y and canceling;

$$\frac{2\,NH_3}{\cancel{2\,NH_4HCO_3}} \times \frac{\cancel{2\,NH_4HCO_3}}{\cancel{2\,NaHCO_3}} \times \frac{\cancel{2\,NaHCO_3}}{Na_2CO_3} \times 1 = Z.$$

Then the number of tons of ammonia sought is

$$\frac{2\,NH_3}{Na_2CO_3} \times 1 = Z;$$

therefore

$$Z = \frac{2\,(17.03)}{106.00} \times 1 = 0.3213 \text{ ton.}$$

It is not necessary to go through all this; the above is offered in proof. These reactions are summed up as follows:

$$2\,NH_3 \equiv 2\,NH_4HCO_3 \equiv 2\,NaHCO_3 \equiv Na_2CO_3;$$

therefore

$$2\,NH_3 \equiv Na_2CO_3,$$

and the ratio is determined.[1]

[1] Another method of arriving at the same result may be exemplified by taking the three equations given above, canceling like molecules on opposite sides of the equality sign and adding:

$$2\,NH_3 + \tfrac{1}{2}\,H_2O + \tfrac{1}{2}\,CO_2 = \cancel{2\,NH_4HCO_3}$$
$$2\,NaCl + \cancel{2\,NH_4HCO_3} = \cancel{2\,NaHCO_3} + 2\,NH_4Cl$$
$$\cancel{2\,NaHCO_3} = Na_2CO_3 + \cancel{H_2O} + \cancel{CO_2}$$
$$2\,NH_3 + 2\,NaCl + H_2O + CO_2 = Na_2CO_3 + 2\,NH_4Cl$$

from which it is at once evident that $2\,NH_3 \equiv Na_2CO_3$.

Factors Other than Chemical. — Factors are of very general application, tables of lengths, weights and other measures coming under this head. Thus, three feet make one yard. The factors are $\frac{3}{1} = 3$ for the conversion of yards into feet and its reciprocal $\frac{1}{3} = 0.333$ is the factor to convert feet into yards. Such examples might be instanced indefinitely. Take the calculation of factors for the conversion of the metric system of lengths into the English system.[1] Having given

Metric system.	English system.
10 decimeters = 1 meter	12 inches = 1 foot
100 centimeters = 1 meter	3 feet = 1 yard
1000 millimeters = 1 meter	5280 feet = 1 mile
1000 meters = 1 kilometer	

and also the fundamental relation, 1 meter = 39.37 inches. The factor for the conversion of meters into feet is

$$\frac{39.37}{12} = 3.2808,$$

which means that 1 meter = 3.2808 feet. Its reciprocal,

$$\frac{12}{39.37} = 0.30480, \quad \text{or} \quad \frac{1}{3.2808} = 0.30480,$$

is the factor for the conversion of feet into meters. In the same way,

$$\frac{39.37}{36} = 1.0936: \text{ factor of meters to yards.}$$

$$\frac{36}{39.37}, \text{ or } \frac{1}{1.0936} = 0.91440: \text{ factor of yards to meters.}$$

then as 1 inch is $\frac{1}{12}$th of a foot and 1 foot = 0.30480 meters,

$$\frac{0.30480}{12} = 0.02540: \text{ factor of inches to meters,}$$

[1] See Chem. Ann., pp. 469–480.

and as 1 meter = 100 centimeters, then 1 inch = 2.540 centimeters. So a table may be constructed:

Given.	Sought.	Factor (or number).	Logarithm.
meters	yards	1.0936	0.03886
yards	meters	0.9144	$\bar{1}$.96114
meters	feet	3.2808	0.51598
feet	meters	0.3048	$\bar{1}$.48402
centimeters	inches	0.3937	$\bar{1}$.59517
inches	centimeters	2.5400	0.40483

PROBLEMS

I. Given the reaction:

$$\underset{278.02}{PbCl_2} + K_2CrO_4 = \underset{323.2}{PbCrO_4} + 2\,KCl.$$

(*a*) What is the factor of lead chloride to lead chromate? (*b*) If 0.1784 g. of lead chromate are precipitated by an excess of potassium chromate from a solution containing lead chloride, how many grams of lead chloride were present? (*c*) How many grams of lead chromate are obtained from 1.000 g. of lead chloride? (*d*) How many grams of lead in 0.7325 g. of lead chromate?

Ans. (*a*) $\dfrac{PbCl_2}{PbCrO_4} = \dfrac{278.02}{323.1} = 0.8605.$

(*b*) $0.1784 \times 0.8605 = 0.1535$ g. $PbCl_2$.

(*c*) $\dfrac{1}{0.8605} = 1.1622$ g. $PbCrO_4$.

(*d*) $\dfrac{Pb}{PbCrO_4} = \dfrac{207.1}{323.1} \times 0.7325 = 0.4695$ g. Pb.

II. Hydrous sodium carbonate may be converted into the anhydrous salt by heat according to the equation:

$$\underset{286.16}{Na_2CO_3 \cdot 10\,H_2O} = \underset{106.00}{Na_2CO_3} + \underset{180.16}{10\,H_2O}.$$

(*a*) How many pounds of anhydrous sodium carbonate may be obtained from 15.000 pounds of the crystallized salt? (*b*)

What is the factor of hydrous sodium carbonate to anhydrous sodium carbonate? (*c*) If 17.000 pounds of hydrous sodium carbonate are converted into the anhydrous form, what is the loss in weight?

Ans.

(*a*) $\frac{Na_2CO_3}{Na_2CO_3 \cdot 10\,H_2O} = \frac{106.00}{286.16} \times 15.000 = 5.5214$ lbs. Na_2CO_3.

(*b*) $\frac{Na_2CO_3 \cdot 10\,H_2O}{Na_2CO_3} = \frac{286.16}{106.00} = 2.6996.$

(*c*) The loss in weight is the water driven off. This problem may be solved in two ways: By using the factor found in (*b*), or by calculating the water directly.

$$\frac{17.000}{2.6996} = 6.2973 \text{ lbs. } Na_2CO_3 \text{ remaining.}$$

$$17.000 - 6.2973 = 10.703 \text{ lbs. water driven off.}$$

Or $\frac{10\,H_2O}{Na_2CO_3 \cdot 10\,H_2O} = \frac{180.16}{286.16} \times 17.000 = 10.703$ lbs. water driven off.

1. (*a*) What is the factor for the conversion $Mg_2P_2O_7 \rightarrow P_2O_5$? (*b*) How many grams of phosphoric anhydride are contained in 0.7256 g. of magnesium pyrophosphate? (*c*) What is the factor for the conversion of $(NH_4)_3\,PO_4 \cdot 12\,MoO_3$ to P_2O_5? (*d*) How many grams of phosphoric anhydride are equivalent to 0.1500 g. of ammonium phosphomolybdate? *Ans.* (*a*) 0.63793.
(*b*) 0.4629 g.
(*c*) 0.03784.
(*d*) 0.005677 g.

2. Verify the following factors:

Given.	Sought.	Factor (number).
K_2PtCl_6	Pt	0.40151
$PbMoO_4$	MoO_3	0.39226
NO	$NaNO_3$	2.8327
$PbSO_4$	Pb	0.68311
$Mn_2P_2O_7$	MnO	0.49961

3. How many grams of chromic sulphide will be formed from 0.7182 g. of chromic oxide according to the equation:

$$2\,Cr_2O_3 + 3\,CS_2 = 2\,Cr_2S_3 + 3\,CO_2?$$

Ans. 0.9460 g.

4. How many grams of tin must be treated with nitric acid to obtain 2 kilos of stannic oxide?

$$Sn \rightarrow SnO_2.$$

Ans. 1576 g.

5. How much charcoal is required to reduce 1.500 g. of arsenic trioxide according to the equation:

$$As_2O_3 + 3\,C = 3\,CO + 2\,As?$$

Ans. 0.2728 g.

6. Iodine is liberated according to the equation:

$$2\,KI + Cl_2 = 2\,KCl + I_2.$$

(*a*) How many grams of iodine are liberated from 0.1726 g. of potassium iodide? (*b*) If 1.5370 g. of iodine are liberated, how many grams of potassium iodide were decomposed?

Ans. (*a*) 0.1319 g.
(*b*) 2.0105 g.

7. Oxygen is prepared from potassium chlorate according to the equation:

$$2\,KClO_3 = 2\,KCl + 3\,O_2.$$

(*a*) What is the yield of oxygen when 7.0680 g. of potassium chlorate are decomposed? (*b*) How many grams of potassium chlorate must be decomposed to get 2.0000 g. of oxygen?

Ans. (*a*) 2.7681 g.
(*b*) 5.1067 g.

8. In the compound $CaCO_3 \cdot 3\,Ca_3(PO_4)_2$, (*a*) how much phosphorus is contained in 5.000 g.? (*b*) How much phosphoric anhydride in the same amount? *Ans.* (*a*) 0.9031 g.
(*b*) 2.067 g.

9. Sulphur dioxide may be produced by the reaction:

$$Cu + 2\,H_2SO_4 = CuSO_4 + 2\,H_2O + SO_2.$$

(*a*) How much copper and (*b*) how much of a 93.20% H_2SO_4 must be taken to obtain 64.00 g. of sulphur dioxide?

Ans. (*a*) 63.50 g.
(*b*) 210.3 g.

10. How much superphosphate can be made from one ton of calcium phosphate, 93.50% pure? The reaction is

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 = 2\,CaSO_4 + CaH_4(PO_4)_2.$$

Ans. 0.7056 ton.

11. Sulphuric acid is made according to the equation:

$$2\,S + 3\,O_2 + 2\,H_2O = 2\,H_2SO_4.$$

(*a*) If brimstone containing 97.00% sulphur is used, how much sulphuric acid is obtained from one ton? (*b*) If pyrites containing 96.00% FeS_2 is used to furnish the sulphur, how many tons are required to yield a ton of sulphuric acid?

Ans. (*a*) 2.9667 tons.
(*b*) 0.6371 ton.

12. Sulphuric acid reacts with sodium hydroxide thus:

$$H_2SO_4 + 2\,NaOH = Na_2SO_4 + 2\,H_2O.$$

If 0.2073 g. of sulphuric acid are added to 0.1705 g. of sodium hydroxide, (*a*) how much sodium sulphate is formed and (*b*) which is left over, caustic or acid, and how much?

Ans. 0.3003 g.
0.0014 g. NaOH.

13. (*a*) What is the percentage of manganese in pure potassium permanganate ($KMnO_4$)? (*b*) If contaminated to an extent of 2.00% of impurities? *Ans.* (*a*) 34.76%.
(*b*) 34.06%.

14. Dolomite is a double carbonate of calcium and magnesium which may in some cases be represented by $CaCO_3 \cdot MgCO_3$. (*a*) What are the percentages of magnesium carbonate and of calcium carbonate in such a sample? (*b*) How many pounds of magnesium carbonate and calcium carbonate in a ton of this

dolomite? (*c*) How many tons of Epsom salts, $MgSO_4 \cdot 7\,H_2O$, can be obtained from a ton of dolomite?

Ans. (*a*) 54.27% $CaCO_3$,
45.73% $MgCO_3$.
(*b*) 1085.4 lbs. $CaCO_3$,
914.6 lbs. $MgCO_3$.
(*c*) 1.337 tons.

15. What are the percentages of the elements in ammonium phosphomolybdate if it is $(NH_4)_3PO_4 \cdot 12\,MoO_3 \cdot 3\,H_2O$?

Ans. N = 2.18%, O = 35.63%,
H = 0.93%, Mo = 59.65%,
P = 1.61%.

16. Regarding ammonium phosphomolybdate as made up of the radicals NH_3, H_2O, P_2O_5 and MoO_3, what is the percentage composition of these radicals in the molecule? See Prob. 15.

Ans. P_2O_5 = 3.69%,
H_2O = 4.20%,
NH_3 = 2.65%,
MoO_3 = 89.47%.

17. Potassium antimonyl tartrate (tartar emetic) corresponds to the formula $K_2H_2(C_4H_4O_6)_2 \cdot Sb_2O_3$. (*a*) What are the percentages of the different elements in this compound? (*b*) What is the percentage of Sb_2O_3? (*c*) How many grams of tartar emetic must be taken to obtain 5.0000 g. of antimony?

Ans. (*a*) K = 11.76%, H = 1.52%,
C = 14.44%, O = 36.11%,
Sb = 36.17%.
(*b*) 43.39%.
(*c*) 13.8245 g.

18. 5.000 g. of arsenic (the metal) are oxidized and the oxide dissolved in caustic potash. How many grams of potassium arsenite are formed? The reactions are

$$4\,As + 3\,O_2 = 2\,As_2O_3,$$
$$As_2O_3 + 6\,KOH = 2\,K_3AsO_3 + 3\,H_2O.$$

Ans. 16.026 g.

19. (*a*) How many pounds of salt are required to make 1500 lbs. of salt cake (Na_2SO_4)? (*b*) How many pounds of Glauber's salt ($Na_2SO_4 \cdot 10\,H_2O$) will this amount of salt cake make? Reactions:

$$2\,NaCl + H_2SO_4 = 2\,HCl + Na_2SO_4,$$
$$Na_2SO_4 + 10\,H_2O = Na_2SO_4 \cdot 10\,H_2O.$$

Ans. (*a*) 1234.4 lbs.
(*b*) 3402.2 lbs.

20. How many grams of ammonium dichromate may be prepared from 500 g. of potassium dichromate according to the reactions:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2\,CrO_3,$$
$$2\,CrO_3 + 2\,NH_3 + H_2O = (NH_4)_2\,Cr_2O_7?$$

Ans. 428.4 g.

21. Iodine may be obtained from potassium iodide according to the equations:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$4\,HCl + MnO_2 = MnCl_2 + 2\,H_2O + Cl_2$$
$$Cl_2 + 2\,KI = 2\,KCl + I_2.$$

How much sulphuric acid must be taken to produce 5.000 g. of iodine? *Ans.* 7.728 g.

22. The Leblanc process for the manufacture of sodium carbonate is

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl,$$
$$Na_2SO_4 + 2\,C = Na_2S + 2\,CO_2,$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

How many tons of sodium carbonate may be obtained from a ton of salt? *Ans.* 0.9066 ton.

23. From the equations:

$$AlCl_3 + 3\,NH_4C_2H_3O_2 = Al\,(C_2H_3O_2)_3 + 3\,NH_4Cl,$$
$$Al\,(C_2H_3O_2)_3 + H_2O = Al\,(OH)\,(C_2H_3O_2)_2 + HC_2H_3O_2,$$
$$2\,Al\,(OH)\,(C_2H_3O_2)_2 + 8\,O_2 = Al_2O_3 + 7\,H_2O + 8\,CO_2.$$

(*a*) How many grams of aluminum chloride are required to yield 0.3000 g. of aluminum oxide? (*b*) How many grams of

aluminum oxide are obtained from 0.8300 g. of aluminum chloride? *Ans.* (*a*) 0.7836 g.
(*b*) 0.3177 g.

24. Chrome iron ore is $Cr_2O_3 \cdot FeO$, and may be converted into potassium dichromate as follows:

$$4\,FeO \cdot Cr_2O_3 + 4\,K_2CO_3 + 4\,CaO + 7\,O_2 = 4\,K_2CrO_4 + 4\,CaCrO_4 + 2\,Fe_2O_3 + 4\,CO_2.$$

The calcium chromate is converted into potassium chromate,

$$CaCrO_4 + K_2SO_4 = CaSO_4 + K_2CrO_4;$$

and potassium dichromate is obtained from potassium chromate,

$$2\,K_2CrO_4 + H_2SO_4 = K_2SO_4 + H_2O + K_2Cr_2O_7.$$

How many tons of potassium dichromate can be obtained from a ton of chrome iron ore, if the conversion is complete and the ore is 92.00% $FeO \cdot Cr_2O_3$? *Ans.* 1.2092 tons.

25. The barometer reads 30.00″. What is the reading in the metric system?[1] *Ans.* 76.20 cm.

26. A piece of aluminum wire 200 mm. long weighs 0.1327 g. What length should be taken to make a centigram rider?
Ans. 15.07 mm.

27. It is required to find the height of a can to hold one quart, the diameter of which must be 4.5″, one half inch being allowed at the top for air space. *Ans.* 4.13″.

28. In estimating the capacity of paint cans, they were filled to within one half inch of the top with water at 60° F. The weights of water were

A, 4.169 lbs.	*C*, 2.084 lbs.
B, 1.042 lbs.	*D*, 8.338 lbs.

What were the capacities of these cans to within one-half inch of the top? (1 gallon = 231 cu. in.) *Ans.* *A*, 2 qts.
B, 1 pt.
C, 1 qt.
D, 1 gal.

[1] The sign (′) is used as an abbreviation for feet, (″) for inches.

29. It is desired to make a 50-cc. burette, graduated to tenths of a cubic centimeter, the graduations to be 2 mm. apart. What should be the diameter of the glass tube? *Ans.* 0.798 cm.

30. Eimer & Amend's catalogue gives the following data about platinum foil: "Platinum foil, medium, $\frac{3}{1000}$" thick, one gram per square inch." Assuming the price of platinum to be \$1.60 per gram, what would a cone for electrolysis cost, having a slant height of 4", diameter 3"? *Ans.* \$30.16.

31. The Westinghouse handbook gives the following data relative to copper wire.

Gage.	Diam. (")	Area sq. in.	Lbs. per 1000 ft.	Ft. per lb.
10	0.10381	0.0081532	31.37	31.38

If one foot = 30.480 cm. and one pound = 453.59 g.: (*a*) What length in centimeters must be taken to weigh 1.500 g.? (*b*) What is the weight in pounds of 7.000 m.?

Ans. (*a*) 3.213 cm.
(*b*) 0.7319 lb.

32. Working up from the datum, one inch = 2.540 cm., verify the following:

Given.	Sought.	Factor.
square centimeters	square inches	0.1550
square inches	square centimeters	6.4516
cubic centimeters	cubic inches	0.06102
cubic inches	cubic centimeters	16.387
square meters	square yards	1.1960
square yards	square meters	0.8361
cubic meters	cubic yards	1.3079
cubic yards	cubic meters	0.7645

33. The internal diameter of a spherical glass bulb is 4.382", what are its contents in cubic cm.? *Ans.* 721.9 cc.

34. A Dumas flask for the determination of molecular weights measures 8.5″ in inner diameter. Neglecting the volume of the drawn-out neck, what is its capacity in liters? *Ans.* 5.27 L.

35. Oil of vitriol is shipped in iron containers. A scow is to be fitted with two tanks running fore and aft. It is able to carry 200 tons of the acid. If the tanks are to be 60′ long, what must be the diameter of the tanks to carry this acid? One cubic foot of oil of vitriol weighs 114.47 lbs. *Ans.* 6.09′.

36. (*a*) How many liters in a cubic foot? (*b*) How many liters in a gallon? (*c*) How many quarts in two liters?

Ans. (*a*) 28.317 L.
(*b*) 3.785 L.
(*c*) 2.113 qts.

37. A circular piece of filter paper 15 cm. in diameter yields 0.00025 g. of ash. (*a*) What will the weight of ash be from a circular piece 5.5 cm. in diameter? (*b*) From a piece of the same kind of paper 3″ square? *Ans.* (*a*) 0.00003 g.
(*b*) 0.00008 g.

38. A tank measures $15.00' \times 20.00' \times 6.00'$. How many liters will it hold? *Ans.* 50,969 L.

39. From the fundamental relation between meters and inches, (*a*) derive the ratio of square feet to square meters, (*b*) square meters to square yards. (*c*) If a wall has an area of 2057 square feet, how many square meters does it contain? (*d*) If cloth costs $2.50 per square meter, what will it cost per square yard? *Ans.* (*a*) 0.09290.
(*b*) 1.1960.
(*c*) 191.1 sq. m.
(*d*) $2.09.

40. (*a*) How many cubic inches in a liter? (*b*) How many cubic meters in an excavation $72' \times 50' \times 12'$?

Ans. (*a*) 61.025 cu. in.
(*b*) 1223.2 cu. m.

41. Derive the value of a kilometer expressed in miles from the fundamental unit; one meter = 39.37 inches.

Ans. 1 km. = 0.62137 mi.

42. A nautical mile is the length of one minute of the earth's circumference at the equator and is equal to 1.1527 statute or land miles. (*a*) What is the circumference of the earth at the equator? (*b*) What is the diameter of the earth at the equator in meters? (*c*) In kilometers? (*d*) How many feet in a nautical mile (knot)?

Ans. (*a*) 24,898 mi.
(*b*) 12,755,000 m.
(*c*) 12,755 km.
(*d*) 6086 ft.

CHAPTER II

APPROXIMATE NUMBERS

An abstract number is accurate as stated, but when a number obtained by measurement represents some multiple of units obtained by measurement or manipulation, it is not absolutely accurate, but only relatively so. This error is called the experimental error or the error of measurement. For example, suppose a substance is weighed on a balance sensitive to a milligram, and equilibrium is established with 1.628 g. as a counterbalance. Should this same weight be determined by a balance sensitive to tenths of a milligram, it cannot be predicted that it will weigh 1.6280 g.; in fact, it may weigh anything between 1.6275 and 1.6285 g. These figures are the extreme limits of variance. The error in weighing on the balance sensitive to a milligram may be less than this; it can only be said with certainty that it is not more. There must be a figure beyond which there is uncertainty. *Such numbers are approximate numbers.* By convention, when a number expresses a multiple of some unit which has been experimentally determined, or derived, it is customary that the last figure given is the last figure known with any degree of certainty. In the example above, the last figure known is 8 in the thousandths place. The uncertainty is ± 5 in the ten thousandths place or ± 0.0005 g. This is the *maximum apparent error.*

A number expressing some multiple of a unit, experimentally determined, or derived, always contains some

error, which is great or small, according to the difficulty, or the delicacy of the operation by which it is determined; hence there must be some figure in the result beyond which there is uncertainty. In atomic weight tables the element iodine will be found stated to five significant figures, while the majority of the atomic weights are given only to three or four significant figures. This is for the reason that this element, a very important one in analytical chemistry, has been very carefully studied, and also because of some of its properties, by taking advantage of which it (the atomic weight) may be determined with the degree of accuracy indicated.

This is the convention, and strictly speaking is seldom accurately followed, as frequently results having an error in the third place are reported as far as the fourth.

There are methods of abbreviated multiplication and division, which eliminate superfluous figures, and indicate the extent to which the result may be relied upon in the use of approximate numbers. Logarithms, however, do all this with the same degree of certainty, and with much less mental fatigue, especially when many extended operations are to be performed. Logarithms themselves are only approximate numbers, and when employed should have a degree of accuracy in their last significant figure equal to, or in excess of, the accuracy of the last significant figure in the approximate numbers involved. For this reason, four- and five-place tables are generally employed, with the balance of opinion in favor of the five-place tables for the usual calculations performed by the chemist. In chemists' handbooks the logarithms of analytical and other factors are given to five places in the mantissa, though many of the figures are reliable only to four places, yet quite as many are accurate to five significant figures. Also, to obtain four significant figures from four-place

tables requires interpolation, while the five-place tables give four figures by direct reading and five by interpolation.[1]

Addition and Subtraction of Approximate Numbers. — It is required to add the following atomic weights, assuming the maximum apparent errors, in order to obtain the molecular weight of aluminum hydroxide, $Al(OH)_3$.

$$\begin{aligned} Al &= 27.1 \\ 3\,O = 3 \times 16.00 &= 48.00 \\ 3\,H = 3 \times 1.008 &= \underline{\ 3.024} \\ Al(OH)_3 &= 78.\underline{1}24 \end{aligned}$$

The last figure (4) in the thousandths place is manifestly uncertain, for the reason that 27.1 has an error of ± 5 in the hundredths place. Strictly speaking, the sum is accurate only to the extent of the tens place, and the result would read 78.1, but the underlined figure is retained for the reason that less error is caused by its retention than by its rejection.[2]

[1] Logarithms have been employed in the solution of problems in this book, except where the operation was very simple. In such cases the 10″ Mannheim slide rule was used. The author would strongly recommend this simple device for the checking of results in the laboratory. It cannot be used exclusively, as the accuracy of the rule is only to three figures in the higher numbers. The mantissa only of a logarithm may be used, neglecting the characteristic, the position of the decimal point being determined by inspection. A chemists' slide rule, manufactured by Kruffel & Esser and devised by the author is now on the market. It is designed to facilitate the computation of such problems as are found in this book and is recommended to students, as by its use much time is saved in calculating the answers to the problems.

[2] This convention has not been strictly followed in the tabulation of molecular weights. See Chem. Ann., pp. 39–47; 100–336. One more figure is carried when the number is to be used in further computation.

Subtraction of approximate numbers leads to the same results.

Multiplication of Approximate Numbers. — Multiplying the number 1.862, containing maximum apparent error, by 0.6257, the results obtained are:

(*a*) By straight multiplication, assuming no errors,

$$1.862 \times 0.6257 = 1.1650534.$$

(*b*) By assuming the maximum apparent error acting in a negative (subtractive) direction,

$$1.8615 \times 0.6257 = 1.16474055.$$

(*c*) By assuming the maximum apparent error acting in a positive (additive) direction,

$$1.8625 \times 0.6257 = 1.16536625.$$

In practice, having a problem of this nature, it is not known whether the error is working in a negative direction (decreasing) as in (*b*) or positive direction (increasing) as in (*c*). If there is any error at all it must be either positive or negative and it is not known which, nor is it known to what extent; it is only known that it is not more than ± 5 in the ten thousandths place; consequently, the most probable result is obtained from (*a*) and is written 1.165, the last figure being uncertain as is seen by an inspection of the results of (*b*) and (*c*).

Again, multiplying 57.2, containing maximum apparent error, by 15.27:

(*a*) Assuming no error,

$$57.2 \times 15.27 = 873.444.$$

(*b*) Assuming the maximum apparent error as being negative,

$$57.15 \times 15.27 = 872.6805.$$

(*c*) Assuming the maximum apparent error as being positive,

$$57.25 \times 15.27 = 874.2075.$$

The result as obtained from (*a*) is 873. It is evident that when a result is obtained by a multiplication involving a unit multiple (approximate number) given to the degree of accuracy adopted by convention, the result may be depended upon only to the same number of significant figures as is contained in the approximate number. It often happens that both the numbers to be multiplied are approximate numbers. Take the case of multiplying 572 and 5725 each containing maximum apparent errors. The result is 3274700 and is reliable only the third figure, for the reason that 572 contains only three significant figures, hence the product is accurate to the same number of places only.

Division of Approximate Numbers. — Take a case of division involving approximate numbers; 5724 contains maximum apparent error, 172 is absolute,

$$(a)\ \frac{5724}{172} = 33.2791\ \ldots : \frac{172}{5724} = 0.0300489\ \ldots$$

$$(b)\ \frac{5723.5}{172} = 33.2762\ \ldots : \frac{172}{5723.5} = 0.0300515\ \ldots$$

$$(c)\ \frac{5724.5}{172} = 33.2821\ \ldots : \frac{172}{5724.5} = 0.0300462\ \ldots$$

Again, if the number which has a maximum apparent error contains only three significant figures, as 152, while 1645 is absolute (contains no error), the following results are obtained:

$$(a)\ \frac{1645}{152} = 10.8223\ \ldots : \frac{152}{1645} = 0.0924012\ \ldots$$

$$(b)\ \frac{1645}{151.5} = 10.8581\ \ldots : \frac{151.5}{1645} = 0.0920972\ \ldots$$

$$(c)\ \frac{1645}{152.5} = 10.7868\ \ldots : \frac{152.5}{1645} = 0.0927051\ \ldots$$

The limit of accuracy, evidently, is the same as in the multiplication of approximate numbers.

Recapitulation. — I. The sum obtained by *adding* approximate numbers is retained to one place beyond the indeterminate figure.[1]

II. *Subtraction* follows the same rule as addition.

III. The result obtained by *multiplication* involving approximate numbers is retained to the same number of significant figures as is contained in the approximate number having the smallest number of significant figures.

IV. *Division* follows the same rule as multiplication.

It does not come within the province of this book to give instruction in the use of logarithms, but a few remarks advocating their use are appropriate. A consideration of approximate numbers shows that results obtained in the manipulation of such numbers are to be depended upon to a degree commensurate with the degree of accuracy of the approximate numbers employed. In most chemical operations, readings are taken to four or five significant figures. Thus a burette is read to four places with the last figure estimated. The average masses determined by the analytical balance seldom exceed six figures, and allowing for tare, the net weight seldom exceeds five, and is generally accurate only to four figures. These approximate numbers, entering as factors into subsequent calculations, carry with them their inherent errors, with the consequence that most results are stated to four significant figures only. In an analysis the constituents are generally given to hundredths of a per cent.

[1] One more figure is carried when the result is to be used in further computation; this applies also for subtraction, multiplication and division.

CHAPTER III

INTERPOLATION

Functions. — When two quantities are interdependent, one is said to be a function of the other. The relation may be very simple, as between pounds and kilograms. An increase of weight in a body of x pounds will cause an increase of y kilograms, x being a function of y. Expressed mathematically, it is $x = ky$. Consequently, knowing the ratio of x to y, x being given, y is readily determined. Let x be the number of pounds and y the number of kilograms change in weight of a system; to convert x pounds into kilograms it is only necessary to multiply by the factor k. In this instance, $k = 0.45359$; so the expression becomes $x = 0.45359\,y$. This is *direct* variation, and by plotting the curve, measuring one of the units along the ordinate and the other along the abscissa, a straight line is obtained. Such curves are seldom plotted.[1]

Graphic Representation of Functions. — Any tabulation, when plotted, yields a curve, the simplicity of which depends upon the particular case under consideration. When two quantities vary *directly* the curve is a straight line;[2] when varying *inversely*, an hyperbola

[1] A tabulation of results obtained by solving the different values of one quantity in terms of the other, where the resulting curve is a straight line, is sometimes contained in handbooks for quick reference.

[2] When the equation is of the first degree, that is, when it does not contain either of the quantities raised to any power other than the first.

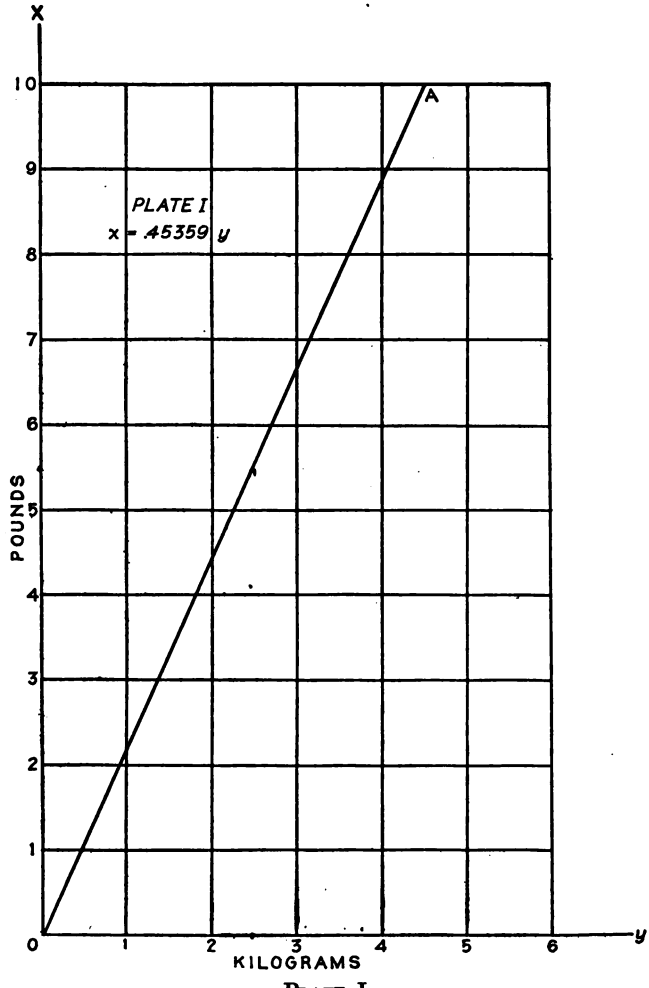

PLATE I.

results. Any value of either x or y, in terms of the other, is as accurately or more accurately obtained by using the factor in the equation under consideration as by consulting the curve.

Plate I represents the curve of pounds equivalent to kilograms; any value of x in terms of y will fall on the line OA.

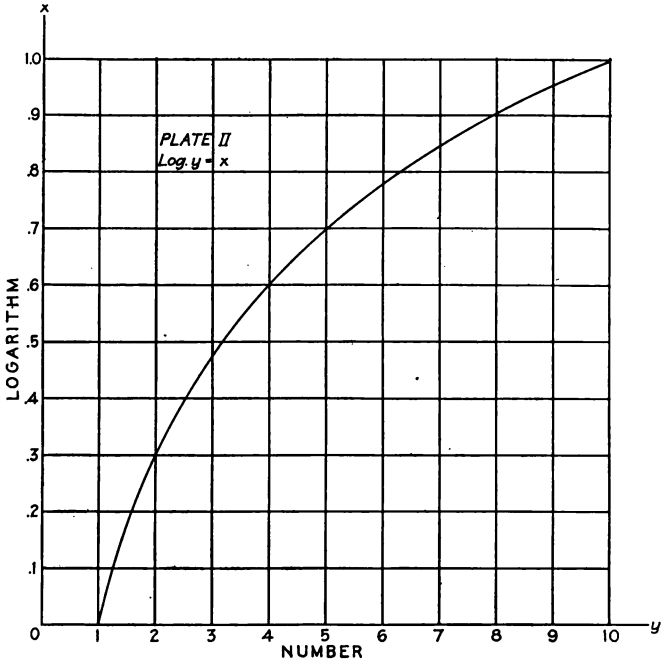

PLATE II.

Plate II represents the relation existing between a number and its logarithm; *i.e.*, the curve fulfils the equation $\log y = x$. (In this case, to obtain values of y in terms of x involves extended mathematical calculations;

consequently these values are determined and once for all tabulated.) Any value of x in terms of y, or vice versa, will fall on the curve.

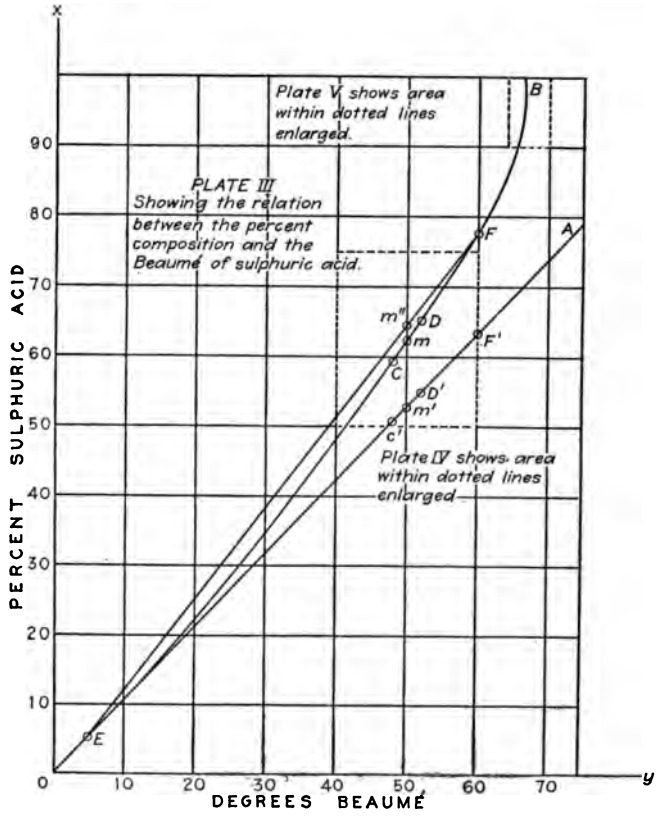

PLATE III.

Change of Percentage Composition with Baumé for Sulphuric Acid. — Plate III shows the relation between the percentage composition and the strength in degrees

Baumé of sulphuric acid.[1] The "Baumé" will be, for the present, used as the weight of a unit volume.[2] An increase in the Baumé of sulphuric acid is accompanied by an increase in the percentage of sulphuric acid (H_2SO_4); so if x represents the percentage of sulphuric acid (H_2SO_4), in a given sample, and y its Baumé, the relation between these quantities is represented by the equation $x = (f)y$.[3]

The distances along the axis OY represent the degrees Baumé (° Bé.) of sulphuric acid and those along OX the percentage composition; if one varied directly as the other a straight line would result. Let 5° Bé. correspond to 5.28% H_2SO_4 (point E), then 60° Bé. would correspond to $\frac{60}{5} \times 5.28 = 63.36\%$ H_2SO_4 (point F'). Connecting these points the curve OA is obtained.

OB is the *true* relationship between degrees Baumé and the percentage sulphuric acid, *determined experimentally;* the curve continually diverging from the straight line OA. Owing to this divergence, acid of 60° Bé. contains 77.67% H_2SO_4 (point F) instead of 63.36%, the percentage calculated on the assumption that the per cent H_2SO_4 varied directly as the Baumé; *i.e.*, that the curve was the straight line OA. This difference, 14.31%, is represented by the distance FF'. The divergence continually increases as the acid approaches 100% H_2SO_4; in fact, as the strength of the acid approaches and passes 93.19% H_2SO_4, corresponding to 66° Bé., a very slight change in the Baumé strength

[1] The data has been taken from the tables of Ferguson and Talbot for Sulphuric Acid. See Chem. Ann., pp. 388–393.

[2] The method of determining the Baumé of a liquid will be discussed at greater length under Specific Gravity, p. 65.

[3] The value of the functions $(f)y$ in the equation $x = (f)y$ in this case varies with the concentration. The value of x corresponding to y must be determined experimentally.

causes a considerable change in the per cent H_2SO_4, the curve approaching perpendicularity. It is for this reason that the method is not employed for acids of a Baumé strength greater than 66° Bé.

Interpolation. — Consider the curve OA included between the points C' and D'; being given:

C' =	48.00° Bé. corresponding to	50.69% H_2SO_4
D' =	52.00° Bé. corresponding to	54.91% H_2SO_4
difference =	4.00° Bé.	4.22% H_2SO_4

It is required to find the per cent H_2SO_4 corresponding to 50° Bé. (point m'); or, having the abscissa of the point m' lying on the line OA, it is required to find its ordinate. The abscissa distance of $C'D'$ is 4.00; the difference between the abscissas of C' and D'. The abscissa distance of $C'm'$ is the difference in Baumé between C' and m'; 50.00° Bé. − 48.00° Bé. = 2.00° Bé. But the abscissa distance of $C'D'$ corresponds to the ordinate distance 4.22; hence the ordinate distance of $C'm'$ is $\frac{2.00}{4.00} \times 4.22 = 2.11$. The ordinate of m' is then $50.69 + 2.11 = 52.80$, the percentage of sulphuric acid corresponding to 50.00° Bé., if these quantities varied according to the curve OA.

This is interpolation. It can only be employed when the curve, between the limits given, may be considered a straight line. The curve OB showing the relation between the Baumé strength and the percentage strength of sulphuric acid has been determined experimentally. It is found to depart considerably from a straight line, but between two points on the curve in close enough proximity the line is sensibly straight.[1] This is shown in Plate IV,

[1] That is, the error is less than the errors of the other factors entering into consideration.

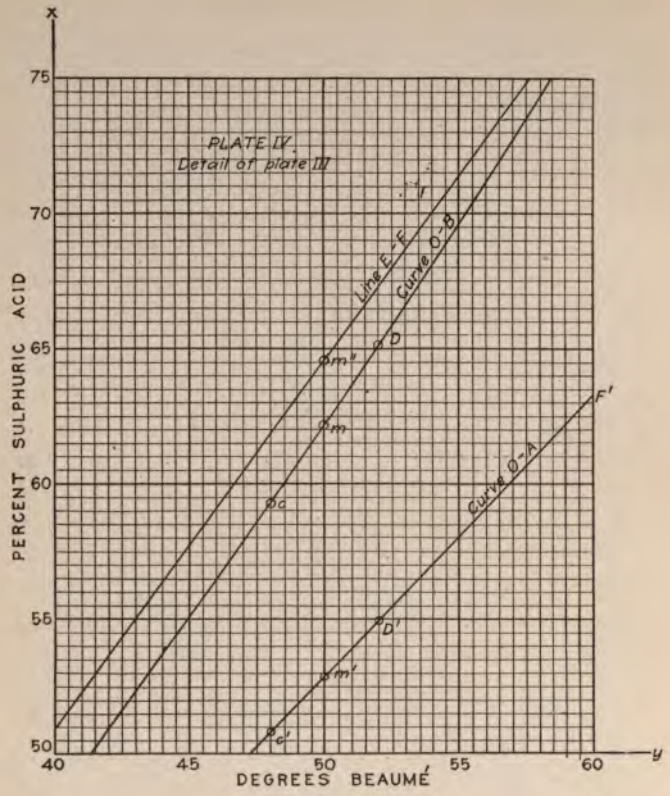

PLATE IV.

an enlargement of a small section of Plate III in the region of $C'D'$.

Working with the curve OB, the following data being given:

C =	48.00° Bé. corresponding to	59.32% H_2SO_4
D =	52.00° Bé. corresponding to	65.13% H_2SO_4
difference =	4.00° Bé.	5.81% H_2SO_4

It is required to find the percentage of sulphuric acid corresponding to 50.00° Bé., or the ordinate of m.[1]

$50.00 - 48.00 = 2.00$ = the abscissa distance of Cm,
4.00 = the abscissa distance of CD,
5.81 = the ordinate distance of CD,

then the ordinate distance of Cm is

$$\frac{2.00}{4.00} \times 5.81 = 2.91,$$

consequently the ordinate of Cm, or the per cent of sulphuric acid corresponding to m, is

$$59.32 + 2.91 = 62.23\%.$$

This value, obtained by interpolation, agrees fairly closely with the value found experimentally, 62.18%; the discrepancy is 0.05%.

Once more, working with the curve OB, given

E = 5.00° Bé. corresponding to 5.28% H_2SO_4
F = 60.00° Bé. corresponding to 77.67% H_2SO_4
difference = 55.00° Bé. 72.39% H_2SO_4

It is required to find the per cent of sulphuric acid corresponding to 50.00° Bé.

$50.00° - 5.00° = 45.00°$ = the excess of ° Bé. of required acid over 5.00° Bé., the ° Bé. below.
$55.00°$ = the interval in ° Bé. between the points given.
72.39% = the interval in per cent H_2SO_4 corresponding to an interval of 55.00° Bé.

$\frac{45.00}{55.00} \times 72.39 = 59.23\%$ H_2SO_4 corresponding to an increase of 45.00° Bé.

$59.23 + 5.28 = 64.51\%$ H_2SO_4 corresponding to 50.00° Bé.

[1] Note that the m' and m correspond to the same Baumé.

This corresponds to point m''. The difference between the per cent of sulphuric acid found by this interpolation, 64.51%, and the per cent of acid found by the previous interpolation, 62.23%, is due to the wide separation of the points (E) and (F) as against the relative proximity of the points (C) and (D) of the previous interpolation, between which intervals the determined curve OB is almost a straight line. m'' must fall on a point in a straight line connecting (E) and (F). The difference, 64.51% − 62.23% = 2.29%, is due to the curvature of OB between the intervals given, and is represented by the distance mm''.

From these considerations, it becomes apparent that to interpolate, the curve must be sensibly a straight line. To obtain this condition, when the curve as a whole deviates from a straight line, the tabular difference must be small enough, or the fixed points near enough, that the curve between the points given is sensibly straight. Consequently, the greater the curvature, the smaller must be the interval between the given points to make the interpolation accurate to the desired degree.

Extrapolation. — Again, working with results experimentally determined (as represented by the curve OB), being given

40.00° Bé. corresponding to	48.10% H_2SO_4
41.00° Bé. corresponding to	49.47% H_2SO_4
difference = 1.00° Bé.	1.37% H_2SO_4

It is required to find the percentage of sulphuric acid corresponding to 42.00° Bé. 42.00° Bé. does not lie between the points given, but it may be calculated if the curve is assumed to be sensibly straight between the intervals 40.00° Bé. and 42.00° Bé.; *i.e.*, if within these limits the Baumé is proportional to the percentage of

sulphuric acid without too much error. On this assumption the percentage of sulphuric acid corresponding to 42.00° Bé. is

$$49.47 + 1.37 = 50.84\%\ H_2SO_4.$$

As a matter of experiment, 42.00° Bé. corresponds to 50.87% H_2SO_4, hence an error has been made of 0.03% H_2SO_4 (50.87 − 50.84) which is relatively small. This is extrapolation and is resorted to with caution for a reason which will appear in the following. Given

65.75° Bé. corresponding to	91.80% H_2SO_4
66.00° Bé. corresponding to	93.19% H_2SO_4
difference = 0.25° Bé.	1.39% H_2SO_4

It is required to find the percentage of sulphuric acid corresponding to 66.25° Bé. On the same assumptions as above, the percentage of sulphuric acid corresponding to 66.25° Bé. is

$$93.19 + 1.39 = 94.58\%\ H_2SO_4.$$

As a matter of experiment 66.25° Bé. is found to correspond to 95.28% H_2SO_4, consequently an error of 0.70% H_2SO_4 (95.28 − 94.58) has been made by extrapolating notwithstanding the small interval taken (0.25° Bé.). In other words, the curve is not sensibly a straight line between the intervals given (65.75° Bé. and 66.25° Bé.). This is shown in the large scale Plate V, page 42.

PROBLEMS

I. Given

60° Bé.[1] corresponding to 77.67% H_2SO_4,

61° Bé corresponding to 79.43% H_2SO_4.

[1] The Baumé is given in the tables to but two significant figures though they are accurate to two places to the right of the decimal point, 60° Bé. being accurate to 60.00° Bé.

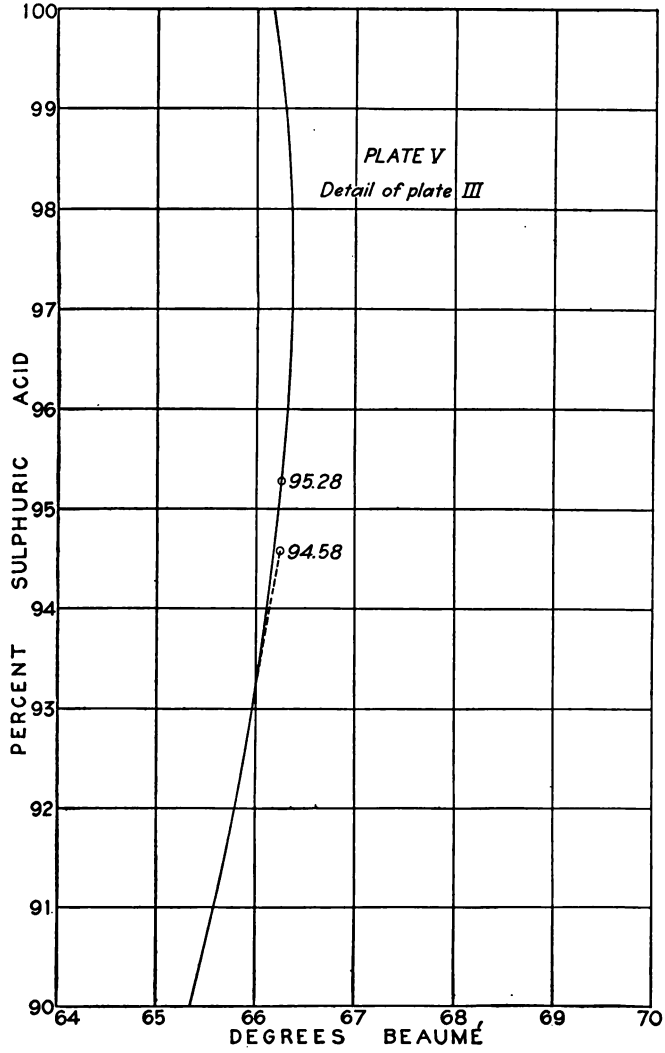
PLATE V
Detail of plate III
95.28
94.58
PERCENT SULPHURIC ACID
100
99
98
97
96
95
94
93
92
91
90
64
65
66
67
68
69
70
DEGREES BEAUMÉ

PLATE V.

(*a*) If the Baumé of a sample of sulphuric acid is 60.85° Bé., what is the percentage of H_2SO_4? (*b*) What is the Baumé of 78.00% sulphuric acid?

Ans. The tabular difference in ° Bé. is 1° Bé. (61 − 60); the tabular difference of per cent H_2SO_4 is 1.76% (79.43% − 77.67%). The increment in ° Bé. of the sample, above the given ° Bé., is 60.85° − 60.00° = 0.85° Bé. Assuming that a small increase in Baumé is accompanied by an increase, in the same ratio, of the percentage of H_2SO_4, the increase of the percentage of H_2SO_4 is

$$\frac{0.85}{1.00} \times 1.76 = 1.50\%.$$

The percentage of H_2SO_4 in the acid is

$$77.67\% + 1.50\% = 79.17\%.$$

(*b*) Analogously,

$$78.00 - 77.67 = 0.33,$$

$$\frac{0.33}{1.76} \times 1.00 = 0.19.$$

60.00 + 0.19 = 60.19° Bé. corresponding to 78.00% H_2SO_4.

II. Given

65.75° Bé. corresponding to 91.80% H_2SO_4,

66.00° Bé. corresponding to 93.19% H_2SO_4.

If an acid is 66.05° Bé., what is its per cent of H_2SO_4?

Ans. It may be assumed that the next interval will be in approximately the same ratio of increase as in the one previous.

Tabular difference is 66.00° − 65.75° = 0.25° Bé.

Tabular difference is 93.19% − 91.80% = 1.39% H_2SO_4.

66.05° − 66.00° = 0.05° Bé.

$$\frac{0.05}{0.25} \times 1.39 = 0.28\% H_2SO_4.$$

93.19 + 0.28 = 93.47% H_2SO_4 corresponding to 66.05° Bé.

At 95.00° C. the pressure of aqueous vapor is 633.78 mm. Hg.[1]
At 96.00° C. the pressure of aqueous vapor is 657.54 mm. Hg.

Ans. 647.09 mm. Hg.

51. In testing the accuracy of a thermometer, the following readings were taken:

Barometric pressure, 652.70 mm. Hg.
Reading of thermometer in melting ice, 0.00° C.
Reading of thermometer in vapor of boiling water, 95.62° C.

Assuming the bore of the thermometer to be uniform and that the barometric pressure exerts no appreciable influence on the melting point of ice, what is the error of the thermometer at these two points? (Use the data given in Problem 50.)

Ans. Correct at 0.00° C.
0.18° C. too low at 95.62° C.

52. The following readings were obtained on a Jolly balance:

Load.	Balance stretches to
0.040 g.	22.0 cm.
0.120 g.	26.2 cm.

If the balance stands at 23.7 cm., what load is in the pan?

Ans. 0.072 gr.

53. Being given the following data on hydrochloric acid:

Sp. gr. 1.155 corresponds to 30.55% HCl.
Sp. gr. 1.145 corresponds to 28.61% HCl.

(*a*) Extrapolate the percentage of hydrochloric acid corresponding to 1.160 sp. gr. (*b*) 1.140 sp. gr. (*c*) The specific gravity of hydrochloric acid containing 31.25% HCl. (*d*) 28.14% HCl.

Ans. (*a*) 31.52%;
(*b*) 27.64%;
(*c*) 1.159 sp. gr;
(*d*) 1.143 sp. gr.

[1] See Chem. Ann., pp. 461–466; also pp. 70–71.

54. Under a pressure of 760 mm. hydrochloric acid (solution) gives a constant boiling point distillate of 20.242% HCl, while under 750 mm. the composition of the distillate is 20.266% HCl. What is the probable composition of a distillate collected under 765 mm. *Ans.* 20.230% HCl.

CHAPTER IV

HEAT

THERE are four units of heat intensity:

I. Fahrenheit (written ° F.). — On the thermometer the melting point of water is marked 32°; the boiling point (b.p.) of water under standard atmospheric pressure (760 mm. Hg) is marked 212°. The distance between these points is divided into 180 (212 − 32) equal spaces, and the same divisions are extended above and below these points. The zero of this scale is 32° (intervals) below the melting point of ice. A change of heat intensity which will cause a change of volume of the substance, usually mercury, through one interval of the scale is a change of one degree Fahrenheit. This scale is used largely in English-speaking countries.[1]

II. Centigrade or Celcius (written ° C.). On the thermometer the melting point (m.p.) of ice is marked 0°;

[1] The expansion of the liquid in the capillary tube is made a measure of heat intensity. The mercurial and other liquid thermometers are based upon the assumption that a change in temperature of any number of degrees is accompanied by a change in the volume of the liquid by a proportionate amount. Through small intervals this is true; the coefficient of expansion of the liquid is sensibly uniform. Mercury, being a liquid, does not exhibit a uniform expansion for a given range of temperature, at all temperatures. Gases, however, more closely approximate a uniform coefficient of expansion, and for this reason the expansion coefficient of hydrogen has been adopted as the standard of temperature measurement. The hydrogen thermometer and the mercury thermometer agree closely in the moderate ranges. See Chem. Ann., pp. 539–541.

the boiling point (b.p.) of water under standard conditions of pressure (760 mm.) is marked 100°. The interval is divided into 100 equal divisions, and the same divisions are extended above and below. This scale is used almost exclusively in scientific work and is common in most Continental countries.

III. Reaumur (written ° R.). — On the thermometer the melting point of ice is marked 0° and the boiling point under standard conditions of pressure (760 mm.) is marked 80°; the interval is divided into 80 divisions. The graduations are extended above and below these points as with the previous scales. This scale is little used except on the Scandinavian Peninsula, in Russia and in some industries.

IV. Absolute (written ° A.). — This scale was derived from observations of the changes of volume of gases accompanying changes of temperature. The scale interval is the same as in the Centigrade system, but the zero is 273° below the melting point of ice. This scale is chiefly used in gas calculations.

The calorie, also called the gram-calorie, is the amount of heat required to raise the temperature of one gram of water one degree Centigrade.[1] This unit is very small and a larger unit, the *big* Calorie,[2] also called the kilogram-calorie (written with a capital C), equal to 1000 gram-calories is often employed.[3]

The British Thermal Unit (written B. T. U.) is the amount of heat required to raise the temperature of one

[1] See Chem. Ann., p. 481.

[2] *Ibid.*, p. 481.

[3] The value of the calorie varies slightly according to the temperature at which it is determined. The amount of heat required to raise one gram of water, at 0° C., one degree Centigrade is not the same as is required to raise the same amount of water at some other temperature, *e.g.*, 15° C., one degree Centigrade.

pound of water at 39.1° F. through one degree Fahrenheit.[1]

Specific Heat. — The number of heat units absorbed by a gram of a substance when its temperature is raised through one degree Centigrade or given up when it falls through one degree Centigrade is called the specific heat of that substance.[2]

When heat passes from one body to another, the amount of heat energy (calories or B.T.U.) gained by the one body is equal to the loss of heat sustained by the other.

The Heat of Fusion (H.F.) is the number of heat units required to change a gram of the substance from the solid to the liquid state without any change of temperature. In the case of ice it requires 80 calories to change one gram of ice at 0° C. to water at the same temperature. The heat of fusion[3] of ice is therefore 80.

The Heat of Vaporization (H.V.) is the quantity of heat required to change a gram of the substance from the liquid to the gaseous state without any change of temperature. In the case of water it is 536.6 calories per gram.

[1] See Chem. Ann., p. 481.

[2] The specific heat of a substance is a ratio of the heat capacity of a unit weight of the substance in question and the heat capacity of the same weight of water which is taken as unity, and is independent of the units of heat measurement employed. The specific heat of magnesium is 0.250; the heat capacity of one pound of magnesium is 0.250 B.T.U.; of one gram of magnesium is 0.250 calories; of one kilogram of the same substance is 0.250 Calories or kilogram-calorie.

For a tabulation of the specific heats of the elements, see Chem. Ann., pp. 4–9. The value of the specific heat of a substance varies with the temperature at which it is measured. In obtaining answers to problems, the specific heat will be assumed to be independent of the temperature of determination.

[3] This term is synonymous with "Latent Heat of Fusion" used by many writers. The term "Latent" is tautologous in view of the definition of the Heat of Fusion.

The Heat of Combustion of a substance may be given in the British or Centigrade systems.[1] In the Centigrade system it is the number of large or small calories evolved from the combustion of a kilogram or a gram of the substance. In the British system it is the number of B.T.U. evolved from the combustion of one pound of the substance.[2]

Conversion of Centigrade into British System Units and Vice Versa. — It follows from the definitions of the different units of temperature,[3] that to convert

° F. to ° C.,	solving $\frac{5}{9}$ (° F. − 32),	gives ° C.
° C. to ° F.,	solving $\frac{9}{5}$ ° C. + 32,	gives ° F.
° F. to ° R.,	solving $\frac{4}{9}$ (° F. − 32),	gives ° R.
° R. to ° F.,	solving $\frac{9}{4}$ ° R. + 32,	gives ° F.
° C. to ° R.,	solving $\frac{4}{5}$ C.,	gives ° R.
° R. to ° C.,	solving $\frac{5}{4}$ ° R.	gives ° C.
° C. to ° A.,	solving ° C. + 273,	gives ° A.
° A. to ° C.,	solving ° A. − 273,	gives ° C.

To convert Fahrenheit or Reaumur to Absolute, first convert to Centigrade and then convert to Absolute.

[1] See Chem. Ann., pp. 481, 502–511.

[2] In American and British mechanical engineering practice, heats of combustion are generally given in B.T.U. This is not considered the best practice by metallurgical engineers, who prefer the kilogram-calorie by reason of its obvious advantages when used in conjunction with the metric system of weights and volumes.

[3] The interval between the melting point of ice and the boiling point of water is 180° for the Fahrenheit scale, 100° for the Centigrade scale and 80° for the Reaumur scale. The zero of the Centigrade and Reaumur scales corresponds to 32° in the Fahrenheit. Hence

$$\frac{\text{F.} - 32}{180} = \frac{\text{C.}}{100} = \frac{\text{R.}}{80}.$$

Solving yields the formulas given above.

From definition, knowing 1 lb. = 453.59 g. and 1° F. = $\frac{5}{9}$° C.:

1 B.T.U. = 453.59 g. of water raised $\frac{5}{9}$° C. = 453.59 × $\frac{5}{9}$
= 252 cal. = 0.252 Cal.

1 Cal. = 1000 g. of water raised 1° C. = 1000 cal. = 1.000 Cal.

Then the factor, given Calories to find B.T.U., is

$$\frac{1.000}{0.252} = 3.96832,$$

and the factor, being given B.T.U. to find Calories, is 0.252 as found above.

The heats of combustion may be converted as follows: Knowing 1 kilogram = 2.2046 lbs., then if the combustion of a kilogram of substance produces X Calories, the fact may be expressed:

	1 kilo.	= X Cal.
or	2.2046 lbs.	= X Cal.;
then for	1 lb.	= $\frac{X \text{ Cal.}}{2.2046}$

and by the factor for the conversion of Calories into B.T.U., found above, the combustion of one pound produces

$$\frac{X\,3.96832}{2.2046} = 1.8000\,X;$$

therefore the factor for the conversion of the heat of combustion of a substance expressed in Calories into the heat of combustion expressed in B.T.U. is 1.8. Conversely, given the heat of combustion of a substance expressed in B.T.U., the factor to convert into Calories is

$$\frac{1}{1.8000} = 0.55556.^{1}$$

[1] A distinction between B.T.U. and Cal. when used in expressing a definite amount of heat and when expressing a heat of combustion must not be overlooked, as these are two different kinds of quantities.

PROBLEMS

I. Convert into Centigrade the following temperatures:

(*a*) 80° F. (*b*) 28° R. (*c*) 250° A.

Ans. (*a*) ° C. = $\frac{5}{9}(80 - 32) = \frac{5}{9}(48) = 26.66°$ C.

(*b*) ° C. = $\frac{5}{4} \times 28 = 35°$ C.

(*c*) ° C. = $250 - 273 = -23°$ C.

II. Convert into Fahrenheit the following temperatures:

(*a*) 60.5° C. (*b*) 40° R. (*c*) 273° A.

Ans.

(*a*) ° F. = $\frac{9}{5} \times 60.5 + 32 = 108.9 + 32 = 140.9°$ F.

(*b*) ° F. = $\frac{9}{4} \times 40 + 32 = 90 + 32 = 122°$ F.

(*c*) ° C. = $273 - 273 = 0°$ C.; ° F. = $\frac{9}{5} \times 0 + 32 = 32°$ F.

III. (*a*) How many calories must have been imparted to 500 g. of water if its temperature is raised from 12° C. to 26° C.? [1] (*b*) How many British thermal units? (*c*) How many Calories?

Ans.

(*a*) $26° - 12° = 14°$ raise in temp.

$500 \times 14 = 7000$ cal.

(*b*) Factor to convert Calories into B.T.U. = 3.96832,

$7.000 \times 3.96832 = 27.778$ B.T.U.

(*c*) 7000 cal. = $\frac{7000}{1000} = 7.000$ Cal.

IV. 200 g. of lead at 100° C. are plunged into 200 g. of water at 0° C., and the resulting temperature is 3.17° C.; what is the specific heat of lead? [2]

Ans.

$200\,(3.17 - 0) = 634$ cal., heat capacity of the lead,

$200\,(100 - 3.17) = 19{,}366$ cal., heat capacity of the water;

[1] Although the value of the calorie varies slightly according to the temperature at which it is defined, this variation will not be considered in the problems in this book. The calorie will be assumed to have a constant value independent of the temperature of definition.

[2] In calculating the specific heats, it will be assumed that the specific heat of the substance under consideration is independent of the temperature, within ordinary ranges.

then as the specific heat is, by definition, the ratio of the heat capacity of the substance compared with the heat capacity of water,

$$\frac{634}{19{,}366} = 0.0327.$$

Or the problem may be solved:

Let X = the specific heat of the lead,
then $200\,X\,(100 - 3.17) = 200\,(3.17 - 0)$;
solving, $X = 0.0327$.

V. If 10 g. of ice at 0° C. are brought into contact with 200 g. of water at 30° C., what is the temperature of the resulting mixture?

Ans.

Let X = final temperature.

80×10 = cal. used to melt the ice without any rise in temp. of the resulting water.

$10\,X$ = cal. used in raising the temp. of this water from 0° C. to X°.

$200\,(30 - X)$ = cal. given up by the water to melt the ice, and to raise the resultant water to temp. X°.

Then as the heat absorbed is equal to the heat given up,

$$(80 \times 10) + 10\,X = 200\,(30 - X),$$

$$X = 24.8° \text{ C.}$$

VI. In the combustion of one gram of a substance, the temperature of 700 g. of water was raised 11.03° C. (*a*) How many Calories were liberated? (*b*) How many Calories per kilogram? (*c*) How many Calories per pound would the substance liberate? (*d*) How many British thermal units per pound?

Ans.

(*a*) $\frac{700 \times 11.03}{1000} = 7.721$ Cal.

(*b*) $7.721 \times 1000 = 7721$ Cal. per kilo.

(*c*) 1 lb. = 453.59 g.; so, $7.721 \times 453.59 = 3502.2$ Cal. per lb.

(*d*) Factor to convert Cal. to B.T.U. = 3.96832,
$3502.2 \times 3.96832 = 13{,}898$ B.T.U. per lb.[1]

[1] It will be noticed that in this problem, starting with the heat given by the combustion of one gram, we have determined the heat of combustion in the British system.

55. The melting point of yellow phosphorus is 44.2° C., and its boiling point is 290° C. What are the corresponding temperatures in Fahrenheit? *Ans.* m. p. 111.6° F., b. p. 554° F.

56. Water is at its greatest density at 4° C. What is this temperature in Fahrenheit? *Ans.* 39.2° F.

57. The average factory temperature is assumed to be 60° F. To what does this correspond in Centigrade? *Ans.* 15.56° C.

58. Sir James Dewar reached a temperature of −264° C. by evaporating liquid hydrogen under diminished pressure. What is this temperature in Fahrenheit? *Ans.* −443.2° F.

59. Zero of the Absolute scale is −273° C. What is the corresponding temperature in Fahrenheit? *Ans.* −459.4° F.

60. Benzaldehyde melts at 7.7° F. and boils at 355.82° F. Find the corresponding temperatures in Centigrade.

Ans. m. p. −13.5° C., b. p. 179.9° C.

61. If the melting point of platinum is 1753° C., what is this in Reaumur? In Fahrenheit? *Ans.* 1402° R., 3187° F.

62. Caproic acid melts at −5.2° C. and boils at 205° C. What are the corresponding temperatures in Reaumur?

Ans. m. p. −4.16° R., b. p. 164° R.

63. Carbon monoxide melts at −168.8° R. and boils at −152° R. What are the corresponding temperatures on the Fahrenheit scale? *Ans.* m. p. −347.8° F., b. p. −310° F.

64. If −271° C. is the lowest temperature so far obtained, what is this temperature in the Absolute scale? *Ans.* 2° A.

65. Given the following:

(*a*) Hydrogen, critical temp. −240°C.; b.p. at atm. press., −251° C.
(*b*) Carbon dioxide, critical temp. 31° C.; b.p. at atm. press., −80° C.
(*c*) Alcohol, critical temp. 243° C.; b. p. at atm. press., 78° C.

What are these temperatures in the Absolute scale?

Ans. (*a*) Crit. temp. 33° A., b. p. 21° A.;
(*b*) Crit. temp. 304° A., b. p. 193° A.;
(*c*) Crit. temp. 516° A., b. p. 351° A.

66. (*a*) At what point is the reading on the Centigrade scale and the Reaumur scale the same? (*b*) Centigrade and Fahrenheit?

Ans. (*a*) 0°;
(*b*) −40°.

67. 100 g. of water at 5° C. are mixed with 100 g. of water at 28° C. What is the temperature of the resultant mixture?

Ans. 16.5° C.

68. What is the resultant temperature when 100 g. of water at 8° C. are mixed with 250 g. of water at 30° C.?

Ans. 23.7° C.

69. On mixing the following quantities of water,

1 kilogram at 30° C.
1.5 kilograms at 25° C.
3 kilograms at 20° C.
4.5 kilograms at 10° C.

what is the temperature of the resultant? *Ans.* 17.25° C.

70. What temperature will result from mixing 15 g. of ice at 0° C. with 300 g. of water at 30° C.? *Ans.* 24.8° C.

71. Equal weights of water and ice at 0° C. are mixed, with the result that the mixture had a temperature of 5° C. What was the temperature of the water? *Ans.* 90° C.

72. If 10 g. of steam at 100° C. are condensed in 100 g. of water at 15° C., what is the resultant temperature? [1]

Ans. 71.5° C.

[1] Authorities differ in the values assigned to the heats of fusion and the heats of vaporization. This may be owing to different temperatures being taken in defining the calorie. The value 80.0 calories will be taken as the heat of fusion of ice in obtaining the answers to the problems in this book. Also 536.6 calories will be taken as the heat of vaporization of water.

73. 150 g. of copper at 100° C. are mixed with 200 g. of water at 12° C. and the resulting temperature is 17.8° C. What is the specific heat of copper? *Ans.* 0.094.

74. 200 g. of mercury at 94° C. are mixed with 200 g. of water at 17° C. and the resulting mixture has a temperature of 19.49° C. What is the specific heat of mercury?

Ans. 0.0334.

75. The specific heat of iron is 0.113. If 100 g. of water at 18° C. are mixed with 150 g. of iron at 65° C., what is the resultant temperature? *Ans.* 24.8° C.

76. When one gram-molecule of carbon combines with two gram-molecules of sulphur to form carbon disulphide, 19,000 calories are absorbed. How many British thermal units are absorbed? *Ans.* 75.39 B.T.U.

77. When two gram-molecules of hydrogen unite with one gram-molecule of oxygen to form water, 68,300 calories are evolved. To how many British thermal units does this correspond? *Ans.* 271 B.T.U.

78. In the reaction

$$CaO + 2\,HCl = CaCl_2 + H_2O,$$

183.45 British thermal units are evolved. To how many Calories does this correspond? *Ans.* 46.23 Cal.

79. The reaction

$$NH_3 + HCl = NH_4Cl$$

liberates 166.27 B.T.U. How many Calories does this correspond to? *Ans.* 41.9 Cal.

80. By the combustion of a certain mass of coal 200 g. of water had its temperature increased from 10° C. to 18.5° C. How many Calories were absorbed? *Ans.* 1.7 Cal.

81. If the combustion of 7 g. of a substance raises the temperature of 500 g. of water from 9° C. to 17.4° C, how many calories are yielded per gram? *Ans.* 600 cal.

82. The heat of combustion of Black Mountain coal is 8333 Calories. What is this in the British system?

Ans. 15,000 B.T.U.

83. The heat of combustion of a sample of coke was found to be 8006 Calories. Convert this into British thermal units.

Ans. 14,411 B.T.U.

84. The heat of combustion of a sample of pine was found to be 9153 British thermal units. What is the value in Calories?

Ans. 5085 Cal.

85. Convert into Calories, 18,718 British thermal units, the heat of combustion of a sample of petroleum.

Ans. 10,399 Cal.

86. The coefficient of expansion of a gas is $\frac{1}{273}$ of its volume at 0° C. for each degree Centigrade of change. What is the coefficient of expansion for a degree Fahrenheit? *Ans.* $\frac{1}{491}$.

87. One gram of a sample of coal raises 700 cc. of water from 6.72° C. to 18.26° C. What is its heat of combustion in British thermal units? *Ans.* 14,540 B.T.U.

88. The combustion of two drams of a substance caused the temperature of 9 ounces of water to be raised 15.43° F. (*a*) What is the heat of combustion in the British system? (*b*) In Calories? (16 drams = 1 oz. avoirdupois.) *Ans.* (*a*) 1111 B.T.U.; (*b*) 617.2 Cal.

CHAPTER V

SPECIFIC GRAVITY

FOR the principles underlying this subject, the student is referred to textbooks on Physics.

The density of a body is defined as the weight of a unit volume, that is

$$\text{density}^1 = \frac{\text{mass}}{\text{volume}},$$

from which it follows that

$$\text{mass} = \text{density} \times \text{volume}$$

and

$$\text{volume} = \frac{\text{mass}}{\text{density}}.$$

The relative density, or specific gravity, of a substance, is the ratio of its mass, referred to the mass of an equal volume of some substance taken as standard. The standard substance for solids and liquids is pure water taken at its maximum density (4° C. or 39.2° F.). Gases have such a low specific gravity referred to water that the weight of a unit volume of a gas is usually referred to the weight of the same unit volume, say either a liter of

[1] The density of a body is the weight of a unit volume. The specific gravity, or the synonymous term, relative density, is the ratio of the density of the body in question, referred to the density of some substance which is taken as unity. In the metric system, the standard employed is water at 4° C. Hence, in this system, the density is numerically equal to the specific gravity (or the relative density). The formulas given are applicable only when the units of measurement are in the metric system.

hydrogen, $\frac{1}{32}$ oxygen, or of air. The specific gravity of gases will be taken up under Gas Calculations.

Specific Gravity of Body Heavier than and Insoluble in Water. — The relative density, or specific gravity, is determined according to the following formula, let

W_b = weight of the body in air,[1]

W_w = weight of an equal volume of water at 4° C.,

then

$$\text{rel. dens. (or sp. gr.)} = \frac{W_b}{W_w}.$$

According to the principle of Archimedes,[2] let

W_b' = weight of the body in water at 4° C.,

then

$$W_w = W_b - W_b',$$

in which $W_b - W_b'$ is the loss in weight in water of a substance heavier than water (*i.e.*, the body is wholly immersed). Hence

$$\text{rel. dens.} = \frac{W_b}{W_b - W_b'},$$

so, to obtain the relative density (or specific gravity), it is only necessary to weigh the substance in air and in water and solve by the formula.

To obtain the relative density when the body is weighed in water at some other temperature than 4° C., say t° C., then

$$\text{rel. dens.} = \frac{W_b}{W_b - W_b'} \times \text{rel. dens. of water at } t\text{° C.}$$

[1] Strictly, this weight should be corrected to weight *in vacuo*. The reduction of the weight in air to the weight *in vacuo* is treated on pages 102–104 of this book. For a fuller discussion, see Chem. Ann., pp. 519–530.

[2] "A body wholly or partly immersed in a fluid (liquid or gas) is buoyed up with a force which is equal to the weight of the volume of the fluid which the body displaces." A Text-Book of Physics, by Duff.

The Specific Gravity of a Solid Substance Lighter than Water is obtained by means of a sinker attached to the solid; the combination being of a relative density greater than water so that it will sink. Let

W_s' = weight of the sinker in water,

W'_{s+b} = weight of the sinker with body attached in water.

Then $$\text{rel. dens.} = \frac{W_b}{W_b + W_s' - W'_{s+b}}.$$

In practice such a determination is most easily carried out by weighing the light substance in air and then weighing the light substance in air suspended from the hook with the sinker attached to it by a slender thread (the sinker being immersed in water) and taking the weight of this combination. Finally, the weight of both the substance and sinker in water is taken. Let

$[W_b + W_s']$ = weight of body in air and sinker in water,

W'_{s+b} = weight of body and sinker, both in water.

Then $$\text{rel. dens.} = \frac{W_b}{[W_b + W_s'] - W'_{s+b}}.$$

The Specific Gravity of Powders is determined by using a specific gravity bottle, flask or pyknometer. The empty bottle is weighed, then filled with water and weighed again. This gives the weight of water held by the bottle. The bottle is emptied and dried and a convenient amount of powder introduced when the bottle and powder are weighed. This gives the weight of the powder. The bottle containing the powder is now filled to the mark and weighed again. Let

W_b = weight of powder taken,

W_{w+f} = weight of flask full of water,

$W_{b+f+\bar{w}}$ = weight of powder, flask and water.

Then $$\text{rel. dens.} = \frac{W_b}{W_b - (W_{b+f+\bar{w}} - W_{w+f})}.$$

Pyknometer Method for Liquids. — The relative density of liquids cannot be obtained by the means outlined above. An obvious method is to compare the weight of a given volume of the liquid in question with the weight of the same volume of water; account being always taken of the temperatures of the two liquids. Then, letting

W_l = weight of a given volume of liquid,
W_w = weight of the same volume of water,

$$\text{rel. dens.} = \frac{W_l}{W_w}.$$

This method is used when extremely accurate results are desired.

Sinker Method for Liquids. — The principle of Archimedes states that a body is buoyed up by an amount equal to the weight of liquid displaced. Knowing the amount of this buoyancy in water and in the liquid the specific gravity of which is to be found, the specific gravity of the liquid can be calculated. The buoyancies are measured by the losses in weight of a solid body in the liquid of unknown density and in water respectively. Any solid (usually a metal) of a specific gravity such that it will sink in both liquids and is not acted upon by either of the liquids will suffice. Let

W_b = weight of the solid body in air,
W_b' = weight of the solid body in water,
W_b'' = weight of the solid body in the liquid whose density is to be determined.

Then

$$\text{rel. dens.} = \frac{W_b - W_b''}{W_b - W_b'}.$$

Constant Weight Hydrometers. — Another method which is based upon the principle of Archimedes is that a body lighter than a liquid in which it is immersed

sinks until it displaces an amount of liquid equal to its own weight. Let

A = area of cross section of a cylindrical floating body,
h = depth to which the cylinder sinks in water,
W_w = weight of water displaced.

In the metric system, the unit of weight, the gram, being the weight of one cubic centimeter of water (at 4° C.), then if A and h are measured in square and linear centimeters respectively, Ah represents a volume of water displaced which is numerically equal to the weight in grams of water displaced. That is

$$W_w = Ah.$$

If the same cylinder is next placed in a liquid of a different density, it will sink to such a depth that it displaces an amount of liquid equal to its own weight. Let

d = the density of this liquid,
h' = the depth to which the cylinder sinks in the liquid,
W_l = the weight of liquid displaced.

The liquid displaced is

$$W_l = Ah'd.$$

Then as equal weights of the liquids are displaced (this is the method of the constant weight hydrometer), $W_w = W_l$, and as the density of water is unity, then

$$Ah'd = Ah, \quad \text{and} \quad d = \frac{h}{h'}.$$

In words, the depth to which a cylindrical floating body will sink is inversely proportional to the density of the liquid in which it is immersed. This is the principle of the hydrometer, which is extensively used commercially.

Constant Volume Hydrometers. — Still another method is the use of the principle of flotation, differing

from the former method in that the volume of hydrometer immersed is constant (that is, that it is immersed to the same depth in the different liquids), the weight of the liquid displaced varying and serving as a measure of the specific gravity. The instrument employed is called the Nicholson's Hydrometer. Let

W_{h+g} = weight of hydrometer plus the weight in grams necessary to be added for it to sink to the mark in water,

$W_{h+\bar{g}}$ = weight of hydrometer plus the weight necessary to be added for it to sink to the mark in the liquid of unknown density.

The weight of the volume of water displaced by the hydrometer when immersed to the mark is W_{h+w}; the weight of the same volume of liquid displaced by the hydrometer when immersed to the mark is $W_{h+\bar{g}}$. This gives the weights of equal volumes, hence [1]

$$\text{rel. dens.} = \frac{W_{h+\bar{g}}}{W_{h+\bar{g}}}.$$

Hydrometers are instruments of glass, weighted at their lower end, the upper end terminating in a thin cylindrical tube. This thin cylindrical tube is graduated, not into lengths, but is calibrated so as to read specific gravity directly.[2] As the density of a liquid changes with the temperature, the liquid should always be at the temperature at which the hydrometer was calibrated or proper correction made. The usual temperature is 60° F. or 15.5° C.

The Baumé Hydrometer is an instrument constructed as a specific gravity hydrometer, but divided into degrees

[1] This same principle is involved in the Westphal's or Mohr balance.

[2] See Chem. Ann., pp. 524–525.

Baumé.[1] These divisions are arbitrary and unscientific, but owing to conservatism and their established use in factories manufacturing heavy chemicals, they are still retained. As in specific gravity determinations, the density of water is taken as unity, but the Baumé scale differs from the specific gravity scale in that, as the density of a liquid decreases below that of water the degrees Baumé increase. For liquids heavier than water an increase in specific gravity is accompanied by an increase in degrees Baumé; consequently it is necessary to know whether the degrees Baumé apply to a liquid heavier or lighter than water.[2]

Conversion of Baumé Readings into Specific Gravity and Vice Versa. — The formulas showing the relations between specific gravity and degrees Baumé for liquids heavier than water are (temp. 60° F.)

$$^{\circ}\text{Bé.} = 145 - \frac{145}{\text{sp. gr.}}.$$

$$\text{Sp. gr.} = \frac{145}{145 - {}^{\circ}\text{Bé.}}.$$

For liquids lighter than water,

$$^{\circ}\text{Bé.} = \frac{140 - 130 \times \text{sp. gr.}}{\text{sp. gr.}} = \frac{140}{\text{sp. gr.}} - 130.$$

$$\text{Sp. gr.} = \frac{140}{130 + {}^{\circ}\text{Bé.}}.$$[3]

[1] See Chem. Ann., pp. 525–526.

[2] For a tabulation of equivalent degrees Baumé and specific gravity for liquids heavier than water, *Ibid.*, pp. 379–383. For liquids lighter than water, *Ibid.*, pp. 383–387.

[3] The Baumé scale as devised by Baumé was graduated in the following manner: The depth to which a hydrometer sank when immersed in a solution made by dissolving 15 parts of pure salt in 85 parts of distilled water was marked 15, temperature 12.5° C. The point to which it sank in pure water was marked 0. The in-

Calculation of Density Determinations to Different Conditions. — In purely scientific calculations, water is taken as standard at 4° C., while in commercial laboratories the standard is often in the neighborhood of 15° C.; consequently specific gravities determined by these standards will not agree. As the temperature of water increases from 4° C., it expands. The weight being constant, with increase of volume, the specific gravity is lowered. In the case of water this increase of volume with rise of temperature is not uniform, but has been determined with great care. Knowing the relative density of water at various temperatures, the volume of a gram is obtained by taking the reciprocal of the density. The expansion of liquids and solids being appreciable, conditions should always be given with densities. This is very important in the case of liquids and differences are appreciable with solids. $D\ \frac{15^\circ}{15^\circ}$ C. is to be interpreted to mean that the temperature of the substance at the time of the determination of its density was 15° C. and that the unit of density is water at 15° C.; $D\ \frac{17.5^\circ}{4^\circ}$ C. means that the temperature of the substance was 17.5° C.

terval was divided into 15 equal parts and the same graduations extended. This is for use with liquids heavier than water. The hydrometer for liquids lighter than water was marked 0 at the point to which it sank in a ten per cent solution of salt and the point to which it sank in pure water was marked 10. The interval was divided into ten equal spaces and the same distances extended. These solutions will not give the exact relations between specific gravity and degrees Baumé cited in the formulas above. The makers of instruments produced so many so-called Baumé hydrometers, no two of which agreed, that the Manufacturing Chemists' Association adopted as the Baumé scale one that will agree with the formulas given above, which is now regarded as standard.

and is referred to water at 4° C.[1] To convert densities of substances taken under one set of conditions into equivalent densities of the same substance under other conditions requires a knowledge of the coefficients of expansion (cubical) of the substance under consideration and water, or what comes to the same thing, the variations in density of the substance and water with change of temperature. For water this has been carefully determined and may be obtained from tables;[2] in the case of other liquids it must be experimentally determined for each individual substance.

To convert $D\,\frac{x^\circ}{y^\circ}$ C. to $D\,\frac{x^\circ}{z^\circ}$ C. requires only a knowledge of the densities of water at $y°$ C. and $z°$ C. Thus, let

$$d = D\frac{x^\circ}{y^\circ}\text{C.} = \frac{\text{weight of unit volume of the body at } x° \text{ C.}}{\text{weight of unit volume of water at } y° \text{ C.}} = \frac{x}{y},$$

$$d' = D\frac{x^\circ}{z^\circ}\text{C.} = \frac{\text{weight of unit volume of the body at } x° \text{ C.}}{\text{weight of unit volume of water at } z° \text{ C.}} = \frac{x}{z},$$

$$d = \frac{x}{y}, \qquad x = dy,$$

$$d' = \frac{x}{z}, \qquad x = d'z,$$

$$dy = d'z,$$

$$d = \frac{z}{y}d', \quad d' = \frac{y}{z}d.$$

[1] Specific gravities may be corrected for the values of the mass factor *in vacuo* (see Tables of Lunge and Isler, Chem. Ann., pp. 394–396) or this correction may be neglected (see Tables of Ferguson and Talbot, *Ibid.*, pp. 388–393). For corrections for weighing in air, see pp. 102–104 of this book. For examples of specific gravities given under specified conditions, see, for example, Aluminum, Chem. Ann., p. 100; Antimony Pentachloride, p. 106, etc.

[2] For changes in the density and volume of water with change of temperature, see Chem. Ann., pp. 457–460.

To calculate $s = \frac{d}{x}$ or $s' = \frac{d'}{x}$ requires a knowledge of the variation in density of the body under consideration with change in temperature. Thus let

$$y = \frac{\text{weight of unit volume of the body at } y^\circ \text{ C.}}{\text{weight of unit volume of water at } x^\circ \text{ C.}} = \frac{y}{x},$$

$$z = \frac{\text{weight of unit volume of the body at } z^\circ \text{ C.}}{\text{weight of unit volume of water at } x^\circ \text{ C.}} = \frac{z}{x},$$

$$d = \frac{1}{x} \qquad s = ky.$$

$$d' = \frac{1}{z} \qquad s = d'z.$$

$$d_1 = d'z$$

$$d = \frac{z}{y}d' \qquad d' = \frac{y}{z}d.$$

PROBLEMS

1. A sample of bismuth weighed 14.738 g. in air and 13.235 g. in water. (a) What is the density of the bismuth? (b) What is the weight of a cube of bismuth 2 cm. in an edge? (c) How many cubic centimeters in a kilogram of bismuth?

Ans. (a) Rel. dens. $= \frac{w_1}{w_1 - w_2}$.

$14.738 - 13.235 = 1.503$ g. loss of weight in water.

$$\frac{14.738}{1.503} = 9.805 \text{ sp. gr.}$$

(b) Mass = rel. dens. × vol.

Mass $= 9.805 \times 2^3 = 78.445$ g.

(c) $\text{Vol.} = \frac{\text{mass}}{\text{sp. gr.}}$.

$$\text{Vol.} = \frac{1000}{9.805} = 101.98 \text{ cc.}$$

[1] For corrections in the case of sulphuric acid, see Chem. Ann., p. 391.

II. A sample of cork weighed 2.140 g. in air. A silver sinker (specific gravity, 10.53) of 10.000 g. was employed, the combination of sinker and cork, in water, weighing 2.274 g. Find the specific gravity of the cork.

Ans. $$\text{Sp. gr.} = \frac{W_b}{W_b + W_s' - W'_{s+b}}.$$

The sinker will displace a volume of water equal to its own volume. The weight of this water will be equal to the loss of weight of the sinker, when weighed in water.

$$\frac{10}{10.53} = 0.9497 \text{ cc.} = 0.9497 \text{ g.}$$

$10.00 - 0.9497 = 9.0503$ g., weight in water of sinker.

Substituting in the formula,

$$\frac{2.14}{2.14 + 9.0503 - 2.274} = \frac{2.14}{8.9163} = 0.2400 \text{ sp. gr.}$$

III. A block of pine weighed 6.431 g. in air. With a sinker attached to the block by a fine thread, the sinker being in water and the block in air, the combination weighed 18.530 g.; the combination of both sinker and block in water weighed 7.635 g. Find the specific gravity of the block of pine.

Ans. $$\text{Sp. gr.} = \frac{W_b}{[W_b + W_s'] + W'_{s+b}},$$

$$\frac{6.431}{18.53 - 7.635} = \frac{6.431}{10.895} = 0.5903.$$

IV. Find the specific gravity of a sample of sand, from the following data: Weight of sand taken, 4.655 g.; weight of bottle full of water, 80.04 g.; weight of bottle containing sand and filled up with water, 82.755 g.

Ans. $$\text{Sp. gr.} = \frac{W_b}{W_b - (W_{b+f+\bar{w}} - W_{w+f})},$$

$$\frac{4.655}{4.655 - (82.755 - 80.04)} = \frac{4.655}{1.94} = 2.399.$$

[illegible]

$$\text{[illegible]} \quad \text{[illegible]} \quad \frac{\text{[illegible]}}{\text{[illegible]}} = \frac{\text{[illegible]}}{\text{[illegible]}}$$

$$\frac{\text{[illegible]}}{\text{[illegible]}} = \frac{\text{[illegible]}}{\text{[illegible]}} = \text{[illegible]}$$

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[illegible] [illegible] specific gravity [illegible] into degrees Baumé. [illegible] [illegible] Baumé hydrometer into specific gravity. [illegible] specific gravity [illegible] into degrees Baumé. [illegible] [illegible] Baumé hydrometer into specific gravity.

Ans.

Substituting in the proper formulas:

$$\text{(a)} \quad {}^{\circ}\text{Bé.} = 145 - \frac{145}{1.7562} = 145 - 82.57 = 62.43^{\circ}.$$

$$\text{(b)} \quad \text{Sp. gr.} = \frac{145}{145 - 45.35} = \frac{145}{99.65} = 1.4552$$

$$\text{(c)} \quad {}^{\circ}\text{Bé.} = \frac{140 - 130}{0.7462} = \frac{140 - 130}{0.7462} = \frac{10}{0.7462} = 33^{\circ}.$$

$$\text{(d)} \quad \text{Sp. gr.} = \frac{140}{130 - 51} = \frac{140}{151} = 0.9735.$$

VII. A liquid shows a specific gravity, $D\ \frac{15.56^{\circ}}{15.56^{\circ}}$ C., of 1.3182. The same liquid shows a specific gravity, $D\ \frac{20^{\circ}}{15.56^{\circ}}$ C., of 1.3142.

[illegible] [illegible] [illegible] specific gravities of elements and chemical compounds, see *Chem. Ann.*, pp. 100–337.

What is the specific gravity, $D\,\frac{17.5°}{17.5°}$ C.? Density of water at 15.56° C. = 0.999040; at 17.5° C. = 0.998713.[1]

Ans.

To change $D\,\frac{15.56°}{15.56°}$ C. (= d) to $D\,\frac{15.56°}{17.5°}$ C. (= d').

$y° = 15.56°$, then $y = 0.999040$,
$z° = 17.5°$, then $z = 0.998713$.

$$d' = \frac{y}{z}d = \frac{0.999040}{0.998713} \times 1.3182 = 1.3196 \text{ sp. gr. } D\,\frac{15.56°}{17.5°}\text{ C.}$$

To change $D\,\frac{15.56°}{17.5°}$ C. to $D\,\frac{17.5°}{17.5°}$ C.

$D\,\frac{15.56°}{15.56°}$ C. = 1.3182

$D\,\frac{20°}{15.56°}$ C. = 1.3142

difference = 0.0040

20° − 15.56° = 4.44°, change in temperature,

$\frac{0.0040}{4.44} = 0.000901$, difference per ° C.

17.5 − 5.56 = 1.94, difference in temperature,

1.94 × 0.000901 = 0.0017.

1.3186 − 0.0017 = 1.3169 specific gravity $D\,\frac{17.5°}{17.5°}$ C.

89. A steel sphere of 1.90 cm. diameter weighed 28.25 g. Knowing that 1 cc. of water at 4° C. weighs one gram, what is the relative density of the steel sphere? *Ans.* 7.866.

90. A block of wood, 7.49 × 7.46 × 3.78 cm., weighs 152.7 g. What is its specific gravity? *Ans.* 0.723.

91. The largest diamond found weighed 3200 carats. If in the form of a cube, what is the length of an edge? (One carat = 205 milligrams; sp. gr. of diamond, 3.530.) *Ans.* 5.706 cm.

92. A footnote in "Pepys' Diary" mentions a stone shot weighing 770 lbs., which fired by the Turks in 1807, struck

[1] See Chem. Ann., pp. 457–458.

H.M.S. "Lion." If spherical and composed of granite (sp. gr., 2.5), what was its diameter? (One cubic foot of water weighs 62.4 lbs.) *Ans.* 25.35 in.

93. Linseed oil has a specific gravity of 0.930. What will it weigh per gallon? (One gallon = 231 cubic inches; one cubic foot of water = 62.37 lbs.) *Ans.* 7.758 lbs.

94. A drum has a capacity of 4 cubic feet. How many pounds of ammonia of 0.8917 specific gravity will it hold? (Take the weight of one cubic foot of water as 62.37 lbs.)

Ans. 222.5 lbs.

95. What is the weight of 15 cubic feet of oil of vitriol, the specific gravity being 1.8354? *Ans.* 1717 lbs.

96. What is the volume of 100 lbs. of hydrochloric acid of 1.2003 specific gravity? *Ans.* 1.335 cu. ft.

97. A casting of iron weighs 1000 kilograms. Taking the specific gravity of iron as 7.23, what is its volume?

Ans. 138 L.

98. A platinum wire 7.25 cm. long weighs 1.0762 g. The specific gravity of platinum is 21.48. Find the diameter of the wire. *Ans.* 0.938 mm.

99. 0.0203 g. of gold (specific gravity = 19.32) was plated on a cubical brass weight 1.5 cm. on an edge. What is the thickness of the gold? *Ans.* 0.00078 mm.

100. What is the radius of a steel sphere (specific gravity, 7.81) equal in weight to a brass sphere (specific gravity, 8.40) 1.5 cm. radius? *Ans.* 1.54 cm.

101. Faraday estimated that the ductility of gold was so high that the gold in four English sovereigns could be drawn into a wire long enough to surround the earth. The weight of a sovereign is 7.988 g., and it contains 91.66% gold. If a quadrant of the earth is 10,000,857 meters, what is the thickness of the wire? (Specific gravity of gold, 19.3.)

Ans. 0.0002198 mm.

102. A casting of iron is suspected of having internal cavities. In air it weighs 170.42 g.; in water 145.60 g. The specific

gravity of cast iron is 7.23. Has the casting any cavities, and if so, what is their volume? *Ans.* 1.25 cc.

103. In obtaining the specific gravity of a sample of heavy spar ($BaSO_4$), the following weights were obtained: Weight in air, 5.127 g.; weight in water, 3.969 g. What is the relative density of the sample? *Ans.* 4.427.

104. In obtaining the specific gravity of a brass weight, the following readings were obtained: Weight in air, 116.62 g.; weight in water, 102.81 g.; temperature of the water, 20° C. (One gram of water expands to 1.001773 cc. at 20° C.) What is the specific gravity of the weight? *Ans.* 8.430.

105. Find the weight of a cubic foot of water at 60° F., knowing that the relative density of water at 60° F. is 0.999050. *Ans.* 62.363 lbs.

106. Calculate the relative density of a block, given:

Weight of block alone in air	152.7 g.
Weight of block alone in air, and sinker in water	218.5 g.
Weight of block and sinker, in water	9.5 g.

Ans. 0.7308.

107. Find the relative density of gutta-percha from the following data: Weight of gutta-percha in air, 4.152 g.; weight of sinker in air, 10.450 g.; weight of sinker in water, 7.546 g.; weight of gutta-percha and sinker, in water, 7.405 g. *Ans.* 0.967.

108. A sample of willow weighed in air 3.820 g. A sinker of lead (specific gravity, 11.4) of a volume of 1.632 cc. was employed, the combination weighing in water 14.26 g. What is the specific gravity of the willow? *Ans.* 0.5843.

109. Determine the relative density of a block of wood from the following data: Weight of block in air, 3.750 g.; weight of lead sinker, 10.000 g.; weight of lead sinker and block under water, 8.315 g. (Specific gravity of lead, 11.34.) *Ans.* 0.824.

110. A platinum ball weighs 19.278 g. in air, 18.382 g. in water and 17.643 g. in sulphuric acid. (*a*) What is the

specific gravity of the platinum ball, and (*b*) of the sulphuric acid? *Ans.* (*a*) 21.52.
(*b*) 1.8248.

111. A specific gravity flask holds 83.327 g. of alcohol of specific gravity 0.8164; 155.79 g. of sulphuric acid, and 120.44 g. of potassium hydrate solution. (*a*) Determine the specific gravity of the sulphuric acid, and (*b*) of the potassium hydrate solution. *Ans.* (*a*) 1.526.
(*b*) 1.180.

112. A piece of glass weighed 5.236 g. in air and its specific gravity was 3.256. It weighed 3.702 g. in a solution of ammonia. Find the specific gravity of the ammonia.
Ans. 0.9539.

113. A cylinder sank 54.40 cm. when immersed in gasoline, and 39.85 cm., in water. What is the relative density of the gasoline? *Ans.* 0.7325.

114. A cylinder was immersed in water at 4° C., and was marked 1.000 at the depth to which it sank. It was then immersed in a liquid of 1.2083 specific gravity, and the depth to which it sank was marked 1.250. The distance between these marks was divided into 25 equal spaces. When the cylinder was placed in a third liquid, it sank to the 1.150 mark; what is the specific gravity of this liquid? *Ans.* 1.125.

115. One side of a U-tube is filled with glycerine, the other with mercury (relative density, 13.6). If 17.4 cm. of mercury balance 187.8 cm. of glycerine, what is the specific gravity of the glycerine? *Ans.* 1.26.

116. A cylinder, when immersed to a certain depth in water, weighed 37.93 g. When immersed to the same depth in gasoline it weighed 27.55 g. What is the relative density of the gasoline?
Ans. 0.7263.

117. Find the specific gravity of the liquid from the following:

Weight of specific gravity bottle.....	40.327 g.
Weight of specific gravity bottle and water..	143.252 g.
Weight of specific gravity bottle and liquid..	108.779 g.

Ans. 0.665.

118. Bunsen gives the following data; from it calculate the relative density of calcium.

Weight of empty bottle	13.64 g.
Weight of bottle filled with naphtha	20.275 g.
Weight of bottle partly filled with naphtha	16.650 g.
Weight of bottle partly filled with naphtha and calcium	19.150 g.
Weight of bottle full of naphtha and calcium	21.576 g.
Relative density of the naphtha	0.758 g.

Ans. 1.58.

119. A sample of bronze is made up of 31.50% zinc, 3.00% tin and 65.50% copper. What is its specific gravity, supposing no change in volume occurred in alloying? (Specific gravities: zinc, 7.142; copper, 8.93; tin, 7.29.) *Ans.* 8.226.

120. A piece of brass weighed 9.0410 g. in water at 4° C. and 10.2621 g. in air. The specific gravity of copper is 8.930 and of zinc is 7.142. What is the per cent of copper and zinc, supposing these two metals, only, are present, and no change of volume took place in alloying? *Ans.* 75.00% Cu, 25.00% Zn.

121. An alloy of gold (sp. gr., 19.32) and silver (sp. gr., 10.53) has a specific gravity of 13.6312. Assuming that no change of volume occurs in alloying, what is its percentage composition (*a*) by volume? (*b*) By weight?

Ans. (*a*) 35.28% Au, 64.72% Ag.
(*b*) 50.00% Au, 50.00% Ag.

122. If the volume of the moon is $\frac{1}{49}$th and its mass $\frac{1}{81}$st that of the earth, (*a*) what is the density of the moon compared to the earth? (*b*) If the relative density of the earth is 5.53, what is the relative density of the moon? *Ans.* (*a*) 0.605. (*b*) 3.34.

123. An amalgam consisting of 60.34% mercury (specific gravity, 13.59) and of 39.66% gold (specific gravity, 19.3) shows

a specific gravity of 15.47. What is the contraction in volume that has taken place in the formation of a kilogram of the amalgam? *Ans.* 0.31 cc.

124. Lupton states that an alloy of 50.00% by weight of platinum (specific gravity, 21.5) and 50.00% by weight of copper (specific gravity, 9.00) has the same color and density as gold (specific gravity, 19.5). What is the contraction in making 50 cc. of the alloy? *Ans.* 26.84 cc.

125. Find the degrees Baumé corresponding to the following specific gravities: (*a*) 1.8354; (*b*) 1.5263; (*c*) 1.2205; (*d*) 0.8963; (*e*) 0.9315. *Ans.* (*a*) 66° Bé.
(*b*) 50° Bé.
(*c*) 26.2° Bé.
(*d*) 26.2° Bé.
(*e*) 20.3° Bé.

126. Find the specific gravities corresponding to the following: Liquids heavier than water; (*a*) 65.75° Bé.; (*b*) 30.6° Bé. Liquids lighter than water; (*c*) 20.85° Bé.; (*d*) 26.92° Bé.
Ans. (*a*) 1.8297 sp. gr.
(*b*) 1.2675 sp. gr.
(*c*) 0.9281 sp. gr.
(*d*) 0.8922 sp. gr.

127. The allowance for temperature, of 13% to 26% nitric acid, is 0.00029 specific gravity, for each degree Fahrenheit. (*a*) Given a sample of acid of specific gravity 1.1154 at 60° F., what is its specific gravity at 45° F.? (*b*) At 78° F. (*c*) What is the weight of 3.4 cubic feet of this acid at 80° F. (*d*) What weight of this acid will occupy 10 cubic feet, at 42° F.? (*e*) What is the volume in cubic feet of 100 lbs. of this acid at 60° F.? (*f*) At 73° F.? (One cubic foot of water at 60° F. weighs 62.37 pounds.) *Ans.* (*a*) 1.1197 sp. gr.
(*b*) 1.1102 sp. gr.
(*c*) 235.3 lbs.
(*d*) 698.9 lbs.
(*e*) 1.437 cu. ft.
(*f*) 1.442 cu. ft.

128. An acid of a certain concentration was found to have a specific gravity of 1.5281 at 56° F., and a specific gravity of 1.5209 at 72° F. (*a*) What is the average expansion per degree F. in cubic centimeters? (*b*) What is the change per degree F. of the specific gravity? (*c*) Change of the strength Baumé per degree F.? (*d*) What is the specific gravity of this acid at 60° F.? (*e*) What is the Baumé strength of this acid at 60° F. (*f*) Assuming the changes of specific gravity and of the Baumé strength to vary uniformly with the temperature, what is the specific gravity of the acid at 50° F.? (*g*) What is the strength Baumé at 80° F.? *Ans.* (*a*) 0.000296.
(*b*) 0.00045.
(*c*) 0.02812.
(*d*) 1.5263.
(*e*) 50.00° Bé.
(*f*) 1.5308.
(*g*) 49.44°.

129. 60° F. is the temperature at which degrees Baumé are tabulated. An acid of a certain concentration changes 0.0235° Bé. for each degree change of temperature (Fahrenheit). (*a*) If the Baumé at 42° F. of a sample of this acid is 66.46° Bé., what is the Baumé at the temperature of tabulation? (*b*) What would be the Baumé of this acid at 73° F.? (*c*) If at 60° F. the per cent of acid corresponding to 66° Bé. is 93.19%, and 65.75° Bé. corresponds to 91.80% acid, what is the per cent acid in this sample? *Ans.* (*a*) 66.04° Bé.
(*b*) 65.73° Bé.
(*c*) 93.41%.

130. A sample of sulphuric acid is 65.25° Bé. at 60° F. How many pounds per cubic foot does it weigh? *Ans.* 113.40 lbs.

131. What must be the diameter of a drum, to hold 400 lbs. of 26° Bé. ammonia (ammonia water), length of drum to be 2.5 feet? (Ammonia is lighter than water.) *Ans.* 1.91 ft.

132. Accurate volumetric analysis requires that correction be made for changes of volume of standard solutions with change of temperature. A solution was standardized at 72° F.

This solution showed a specific gravity of 1.0277 at 84° F., and 1.0378 at 40° F. (*a*) What is the expansion per unit volume per degree Fahrenheit? (*b*) If a determination was made with this solution at 55° F., using 98.00 cc., what correction must be made to find what the volume would be at 72° F., the temperature at which it was standardized? (*c*) What is the volume corrected to 72° F.? *Ans.* (*a*) 0.000225.
(*b*) + 0.37 cc.
(*c*) 98.37 cc.

133. The specific gravity, $D\ \frac{15°}{4°}$ C., of a 70% mixture of alcohol and water (by weight) is 0.87187. The specific gravity, $D\ \frac{20°}{4°}$ C., is 0.86766 for the same mixture. (*a*) Calculate $D\ \frac{17.5°}{4°}$ C. and (*b*) $D\ \frac{15°}{15°}$ C. for this liquid. Density of water at 15° C. = 0.999126. *Ans.* (*a*) 0.86976.
(*b*) 0.87264.

134. The specific gravity, $D\ \frac{15.56°}{15.56°}$ C., of 50.87% H_2SO_4 is 1.4078. (*a*) What is the specific gravity, $D\ \frac{15.56°}{4°}$ C.? (*b*) $D\ \frac{15°}{4°}$ C.? Sulphuric acid of this concentration decreases 0.000738 $D\ \frac{15.56°}{15.56°}$ C. for each ° C. Density of water at 15.56° C. = 0.999040. *Ans.* (*a*) 1.4065.
(*b*) 1.4069.

135. Nitric acid containing 50.32% HNO_3 has a specific gravity, $D\ \frac{15.56°}{15.56°}$ C., of 1.3182. The same acid shows a specific gravity, $D\ \frac{20°}{15.56°}$ C., of 1.3134. What is the specific gravity, $D\ \frac{17.5°}{17.5°}$ C.? Density of water at 15.56° C. = 0.999040; at 17.5° C. = 0.998713. *Ans.* 1.3165.

136. The Baumé, $D\ \frac{15.56°}{15.56°}$ C., of 77.67% H_2SO_4 is 60.00°. This same acid shows a Baumé, $D\ \frac{20°}{15.56°}$ C., of 59.79°. What is the Baumé, $D\ \frac{15°}{4°}$ C.? *Ans.* 59.97° Bé.

137. Calculate the difference in specific gravity in the tables of Ferguson and Talbot and those of Lunge and Isler on an acid of 50.00% H_2SO_4, being given the following:

Ferguson and Talbot

49.47% H_2SO_4 = 1.3942, $D\ \frac{15.56°}{15.56°}$ C.

50.87% H_2SO_4 = 1.4078, $D\ \frac{15.56°}{15.56°}$ C.

Lunge and Isler

50.11% H_2SO_4 = 1.4000, $D\ \frac{15°}{4°}$ C.

50.63% H_2SO_4 = 1.4050, $D\ \frac{15°}{4°}$ C.

Density of water at 15.56° C. = 0.999040.

Correction for 50% H_2SO_4 = 0.000738 $D\ \frac{15.56°}{15.56°}$ C. for each ° C.

Ans. L. and I., 0.0023 sp. gr. lower.

CHAPTER VI

GAS CALCULATIONS

Boyle's Law. — The temperature remaining constant, the volume of a gas varies inversely as the pressure to which it is subjected. Let V be the volume of a gas under a pressure P, and let V' be some other volume of the same quantity of the gas and P' its corresponding pressure. The analytical expression of this law is

$$\frac{V}{V'} = \frac{P'}{P},$$

or

$$PV = P'V'.^{1}$$

Charles' Law. — The pressure remaining constant, the volume of a gas varies directly as the absolute temperature to which it is subjected. Let V be the volume of a gas at a temperature T, and let V' be some other volume of the same quantity of the gas and T' its corresponding temperature. Then the analytical expression of this law is

$$\frac{V}{V'} = \frac{T}{T'}.^{2}$$

Since 0° C. corresponds to 273° A., the law of Charles may be stated: The pressure remaining constant, a true

[1] $P'V' = k$, a constant, therefore on plotting the changes of a given volume of a gas under varying pressure or temperature an hyperbola results.

[2] Note that T and T' are in the absolute temperature scale.

gas expands or contracts $\frac{1}{273}$ of its volume at 0° C., for each degree Centigrade rise or fall in temperature.[1]

Furthermore, the volume remaining constant, the pressure on a gas varies directly as the absolute temperature. Let P be the pressure of a gas at temperature T and let P' be some other pressure on the same quantity of the gas and T' its corresponding temperature. Then the analytical expression of this fact is

$$\frac{P}{P'} = \frac{T}{T'}.$$

The gas thermometer is based upon this law. The standard degree of temperature is a temperature interval such as will cause the pressure on a confined gas to change $\frac{1}{100}$ of that change in pressure which is shown by a true gas between the temperature of melting ice and the temperature of water boiling under standard pressure. Thus, the pressure exerted by a gas is used as a means of measuring temperature, and is employed in the hydrogen thermometer, in which the volume is kept constant and differences of pressure caused by different temperatures are measured. This unit has been chosen for the reason that the expansion coefficient of hydrogen is very uniform over wide ranges of temperature, a property of all gases in a condition far removed from their liquefaction point. Mercury, being a liquid, does not expand with this regularity with increase of temperature, although at

[1] $\frac{1}{273}$ may be expressed as a decimal, when it becomes 0.003663. Every gas has its own coefficients of expansion, one under constant pressure, which is the coefficient usually required for gas calculations, the other under constant volume, a coefficient of a different numerical value. For air the coefficient has been found to be 0.0036706 (under constant pressure) and the decimal value 0.00367 is usually employed for every gas where extreme accuracy is not required. See Chem. Ann., p. 73.

ordinary temperatures the difference between a temperature reading with a hydrogen thermometer and with a mercury thermometer is slight.[1]

Laws of Boyle and Charles Combined. — The laws of Boyle and Charles are readily combined in one expression. Considering a given weight of gas, Boyle's law is

$$P \propto \frac{1}{V}, \quad \text{hence} \quad P = K\frac{1}{V},$$

in which K is a constant. The law of Charles is

$$P \propto T, \quad \text{hence} \quad P = K'T,$$

in which K' is a constant. Combining these expressions:[2]

$$P = r\frac{T}{V}, \quad \text{or} \quad \frac{PV}{T} = r,$$

in which r is a constant for the same quantity of gas. From this it follows that the same mass of gas under the conditions P', V' and T' gives

$$\frac{P'V'}{T'} = r;$$

hence

$$\frac{PV}{T} = \frac{P'V'}{T'}.$$

[1] Gases only conform to these generalizations approximately. In general, the further a gas is removed from its liquefaction temperature, the more closely does it obey the gas laws. An "ideal" gas is a hypothetical gas which is supposed to exactly obey the gas laws. A distinction between gases and vapors is sometimes made, assigning to the former a condition of temperature above its critical temperature, and to the latter a condition of temperature below its critical temperature.

[2] If the volume varies inversely as the pressure and directly as the absolute temperature, then the product of the volume into the pressure is equal to the absolute temperature into a constant. When a gram molecular volume (G.M.V.) is under consideration, this is usually expressed, $PV = RT$.

Knowing five of these quantities, the sixth may be obtained by solving the equation. It is more to be recommended, however, that in solving gas equations the logic of the case should serve as a guide than that a formula should be used unthinkingly. For example, a volume of a gas equal to V at a temperature T is to be changed to temperature T', pressure remaining constant. Knowing that a gas expands with a rise and contracts with a fall of temperature, a ratio may be made employing T and T' which is a proper or an improper fraction according as the gas contracts or expands. This ratio is multiplied by V to obtain V'. The same may be said for changes of volume of gases with change of pressure, temperature remaining constant. Let V be the volume of a gas at pressure P, which is to be changed to pressure P'. The new volume V' will be found by using P and P' as terms of a ratio, recollecting that if the new condition of the gas is to be a smaller volume than V, the ratio must be in the form of a proper fraction; if larger, an improper fraction. This fraction is multiplied by V to obtain V'.

Standard Conditions of Pressure and Temperature. — As changes of temperature and pressure exert so considerable an influence upon the volume of a gas and consequently upon the weight of a unit volume, standard conditions have been adopted, which are: 0° C. as standard temperature, and a pressure equal to that exerted by a column of mercury 76 cm. high when at a temperature of 0° C.[1] The measurement of temperature has already been discussed; it remains to take up the measurement of pressure. Pressure is usually expressed as so many units of weight per square unit of area. Atmos-

[1] See Chem. Ann., p. 3.

pheric pressure is measured by the height of a column of mercury which will balance this downward pressure of the atmosphere. Then if the height of the mercury column is taken to be standard at 76 cm. at a temperature of 0° C. and the specific gravity of mercury is 13.596 at this temperature, the pressure per square centimeter is $13.596 \times 76 = 1033.3$ g. As atmospheric pressure is always measured by a mercury barometer or a barometer standardized against a mercury barometer, it is only necessary to indicate the height of the column of mercury.

Correction of Barometer for Temperature. — Mercury expands and contracts with rise and fall of temperature; consequently its specific gravity increases and decreases. So, merely measuring the height of the column of mercury is not an exact measurement of the pressure. As 0° C. is the standard of temperature of a gas, so also is this same temperature taken at which the height of the mercury column is standard. For example, at 0° C. the specific gravity of mercury is 13.596, then the pressure of 76 cm. of mercury at this temperature is $76 \times 13.596 = 1033.296$ g. per square centimeter. At 15° C. the specific gravity of mercury is 13.560, then the pressure of 76 cm. of mercury at this temperature is $76 \times 13.560 = 1030.56$ g. per square centimeter. The height of the column of mercury is usually measured by graduations on the glass, or the glass tube is mounted in a brass jacket which carries the graduations. If the expansion of the mercury and of the substance carrying the graduations were the same, no correction for temperature in reading the barometer would be necessary; because, as the mercury expanded, though its specific gravity would be lowered, the material carrying the graduations would expand by an equal amount and these expansions would neutralize each

other, as the graduations would register a greater length than the true length.[1]

As an expansion of the mercury is accompanied by an expansion of the material carrying the graduations, it is only necessary to determine the difference between the coefficient of expansion of the mercury and its containing tube. This is the apparent expansion of the mercury, and for measuring this height on a glass tube 0.00017 of the column at 0° C. for each degree departure from this temperature is the correction. For a brass scale it is 0.00016. Hence $1 \pm at$ is the length of the apparent column as compared with the column at 0° C. In this expression a is the apparent coefficient of expansion and t is the number of degrees from 0° C. Then if P is the observed height of the barometer, the corrected reading is $\frac{P}{1 \pm at}$.[2]

Moist Gases. — Volumes of gases are often measured over liquids which may or may not exert an appreciable vapor pressure. The vapor pressure of a saturated vapor depends upon the temperature only, and is independent of the pressure or the presence or absence of an inert gas. If a sufficient amount of a volatile liquid is introduced into a Torricellian vacuum above the mercury in a barometer or into a barometer tube containing a gas, the height of the mercury column will be depressed by an amount which is independent of all conditions except the temperature. If, then, the volume of a confined gas is measured

[1] For the very accurate reading of some forms of the mercury barometer, capillarity must also be taken into account. This correction will not be considered here as it varies with the form of the instrument and the diameter of the tube. This correction is usually supplied by the manufacturer with each instrument.

[2] For a fuller discussion, see Chem. Ann., pp. 542–543.

over a volatile liquid such as water, the volume will appear greater than the volume of the same amount of dry gas by an amount corresponding to the vapor pressure of the water (if this be the liquid employed)[1] at that temperature. If this vapor pressure were a constant quantity or increased regularly with rise in temperature, it would be a simple matter to correct for it; but such not being the case, the vapor pressures corresponding to various temperatures are determined experimentally and tabulated.[2] Let

P_{g+w} = the pressure of the moist gas,
P_w = the pressure of the water vapor,
V_{g+w} = the volume of the moist gas,
V_g = the volume of the dry gas.

Then $P_{g+w} - P_w$ is the pressure of the dry gas, the volume of which is

$$V_g = \frac{P_{g+w} - P_w}{P_{g+w}} V_{g+w}.$$

When measuring a gas over mercury, whether moist or not, a common procedure is to bring the mercury to the same level inside and outside the tube, the pressure of the gas being that indicated by the barometer. It may not be convenient to do this; then, to measure the pressure of a gas confined in this way, the height of the mercury in the tube must be subtracted from the barometric reading.[3]

[1] Every liquid has a vapor pressure which is peculiar to that liquid. To determine the variation of vapor pressure of a liquid with change of temperature is a matter of experiment.

[2] For the values for water, see Chem. Ann., pp. 461–466.

[3] If the gas is measured over some liquid other than mercury and the level inside and outside the tube is not the same, the height of the liquid must be reduced to the equivalent height of a column of mercury. This necessitates a knowledge of the specific gravities of the mercury and the liquid.

Let

P_b = the pressure indicated by the barometer,

P_h = the height of mercury in the tube.

Then the pressure of the moist gas is $P_b - P_h$ and the pressure of the dry gas is $(P_b - P_h) - P_w$, or $P_b - (P_h + P_w)$, and the volume of the dry gas is

$$V_g = \frac{P_b - (P_h + P_w)}{P_{g+w}} V_{g+w}.^1$$

Gay-Lussac's Law of Combination by Volume. — In a chemical combination of gases, producing a gas, there is always a simple ratio between the volumes of the factors (the gases entering into the reaction) and the volumes of the products (the gas or gases resulting). Chemical equations represent not only combination by weight, but also combination by volume. From the equation

[1] Tables are constructed for reducing the volume of a gas, moist or dry, to the volume which the gas would occupy dry at standard conditions (0° C. and 760 mm.). For example, 300 cc. of a gas is measured moist at 18° C. and 765 mm. What is the volume, dry, at 0° C. and 670 mm.? Using the decimal coefficient, the expression to solve is $V_g = \frac{1}{1 + (18 \times 0.00367)} \times \frac{765 - P_w}{760} \times 300$. The logarithm of the factor $\frac{1}{760(1 + 0.00367\,t)}$ and the values of P_w for different temperatures are given in the table. To solve by use of the table:

$\log \frac{1}{760\,(1 + 0.00367\,t)}$ for 18° C. $= \bar{3}.09141$

Ten. aq. vap. for 18° C.
= 15.38 mm.; 765 − 15.38 = 749.62; log = 2.87484

log 300 = 2.47712

sum of logs = $\overline{2}.44337$

antilog = 277.57

This considerably simplifies the calculation. See Chem. Ann., pp. 70–71.

	$2\,H_2O$	=	$2\,H_2$	+	O_2
(*a*)	36.032		4.032		32
(*b*)	2 vols.		2 vols.		1 vol.

the subscripts (*a*) give the decomposition by weight, while subscripts (*b*) indicate the volumes entering into the reaction. It is to be noted that in writing equations from which calculations involving volumes are to be made, care must be taken to represent the molecular condition of the gases. When this is done the coefficients of the symbols indicate the volumes of factors and products.

Gas Analysis. — Gay-Lussac's law finds constant application in gas analysis. Given a mixture of hydrogen, carbon monoxide and methane; the mixture may be analyzed by exploding the whole with an excess of oxygen and noting the contraction. The resulting carbon dioxide is next absorbed in potassium hydroxide and the contraction again noted. The reactions taking place are:

(*a*)	$2\,H_2$	+	O_2	=	$2\,H_2O$			
	2 vols.		1 vol.		0 vol.			
(*b*)	$2\,CO$	+	O_2	=	$2\,CO_2$			
	2 vols.		1 vol.		2 vols.			
(*c*)	CH_4	+	$2\,O_2$	=	CO_2	+	$2\,H_2O$	
	1 vol.		2 vols.		1 vol.		0 vol.	

In regard to the contraction caused by oxidation, the following is to be noted:

Reaction (*a*) shows that *two* volumes of water vapor and *one* volume of oxygen, in all *three* volumes, disappear in the oxidation of *two* volumes of hydrogen (the water vapor being condensed to a liquid, the volume of which may be neglected, being approximately only $\frac{1}{1700}$ of the volume it occupies as steam). Then, if x represents the volume of hydrogen originally present, $\frac{3}{2}\,x$ is the amount of contraction due to the oxidation of hydrogen.

Reaction (*b*) shows that where originally there were *three* volumes of gas present before the explosion, *two* volumes of carbon monoxide and *one* volume of oxygen, after oxidation there remain only *two* volumes of carbon dioxide, a net loss of *one* volume. If y represents the volume of carbon monoxide originally present, $\frac{1}{2}y$ represents the contraction due to the oxidation of carbon monoxide.

Reaction (*c*) shows that where originally there were *three* volumes, *one* volume of methane and *two* volumes of oxygen, after explosion there remains but *one* volume, the loss in this case being *two* volumes. As this contraction was caused by *one* volume of methane, then, if z represents the volume of methane originally present, the contraction due to methane is $2z$.

After exploding the mixture, the resulting carbon dioxide is absorbed by potassium hydroxide, the reaction being

$$CO_2 + 2\,KOH = K_2CO_3 + H_2O.$$

Reaction (*a*) produces no carbon dioxide, hence no part of the carbon dioxide absorbed can be ascribed to hydrogen.

Reaction (*b*) shows that carbon dioxide to the extent of *two* volumes will be absorbed by the potassium hydroxide, and as these *two* volumes of carbon dioxide resulted from *two* volumes of carbon monoxide, it is evident that, if y be the volume of carbon monoxide originally present, the same volume will be absorbed.

Reaction (*c*) shows that *one* volume of carbon dioxide is absorbed which was produced from *one* volume of methane. If z represents the volume of methane originally present, the contraction, due to the absorption of carbon dioxide produced from z volumes of methane, will be z.

To put these facts in algebraic form, let

A = volume of mixture taken,
B = volume of contraction after explosion,
C = volume of carbon dioxide absorbed,
x = volume of hydrogen,
y = volume of carbon monoxide,
z = volume of methane.

(*a*) $A = x + y + z.$
(*b*) $B = \frac{3}{2}x + \frac{1}{2}y + 2z.$
(*c*) $C = y + z.$

(*a*) $A = x + y + z.$
(*c*) $C = y + z.$
(*d*) $A - C = x.$ (by subtraction.)

Substituting the value of (*d*) in (*a*), clearing (*b*) of fractions and solving:

(*e*) $A = A - C + y + z.$
(*b*) $2B = 3A - 3C + y + 4z.$

$A - 2B = -2A + 2C - 3z.$ (by subtraction.)

(*f*) $z = \frac{-3A + 2B + 2C}{3}.$

Substituting (*f*) and (*d*) in (*a*) and solving for y:

$$A = A - C + y + \frac{-3A + 2B + 2C}{3},$$

$$3A = 3A - 3C + 3y - 3A + 2B + 2C.$$

$$y = \frac{3A - 2B + C}{3}.$$

Avogadro's Law. — Equal volumes of gases, elementary or compound, at the same temperature and pressure, contain the same number of molecules.

This law gives a method of determining molecular weights. Let n be the number of molecules of gas A, and

m the weight of each molecule, then the total weight w of this gas is

$$w = nm.$$

Also let m' be the weight of each molecule of another gas B of the same volume and under the same conditions of temperature and pressure, then the weight w' of this gas is

$$w' = nm';$$

the ratio of the weight w to w' is

$$\frac{w}{w'} = \frac{nm}{nm'};$$

consequently,

$$\frac{w}{w'} = \frac{m}{m'},$$

or the ratio of the molecular weights of two gases is the ratio of the weights of equal volumes under the same conditions. So if B is the gas taken as standard, the molecular weight m of the gas A is w, or the weight of a unit volume of the gas A referred to the weight of the same volume in the same condition as the gas B.

Atomic Weights and Molecular Weights. — Hydrogen was the gas formerly taken as the basis of atomic weights; but lately an ideal gas of a weight $\frac{1}{32}$ of oxygen gas has come into almost universal acceptance. For practical purposes air is often used in determining molecular weights. From what has been stated it is evident that these gases bear the same relation to the determination of molecular weights as water bears to the determination of specific gravity. As one cubic centimeter of water at 4° C. is taken as the unit weight of a unit volume in specific gravity determinations, so in molecular weight determinations, which are analogous, the unit

of weight is the weight, under standard conditions, of one liter of hydrogen, $\frac{1}{32}$ of the weight of oxygen gas, or, lastly, the weight of one liter of air.

Atomic weights are now based on oxygen as 16, and as a molecule of oxygen is composed of two atoms, the molecular weight of oxygen is 32, so the unit in atomic weights is $\frac{1}{32}$ of the weight of oxygen gas.[1]

One liter of oxygen, at sea level, latitude 45°, under a pressure of 760 mm. of mercury and at 0° C. weighs 1.4290 g. Hence one liter of an imaginary gas having a unit atomic weight would weigh, per liter,

$$\frac{1.4290}{32} = 0.044656 \text{ g.}$$

Consequently, if m is the molecular weight of any gas, $0.044656\, m$ = weight of a liter under standard conditions, and, conversely, given the weight w of a liter of gas under standard conditions, the molecular weight m is

$$m = \frac{w}{0.044656}.$$

Instead of dividing the weight of a liter of the gas by 0.044656 it may be multiplied by the reciprocal 22.393. In general terms the relation between the weight w of a liter of gas and its molecular weight m is

$$w = \frac{m}{32} \times 1.4290 = 0.044656\, m \text{ g.}$$

Vapor Density. — Relative density being defined as the ratio of the weight of a unit volume of the substance under consideration referred to the weight of the same

[1] Most of the common elementary gases have two atoms in the molecule. Examples: Cl_2, H_2, N_2, etc. See Chem. Ann., p. 3.

volume of another substance taken as standard,[1] the formula for relative density is

$$\text{Density to standard substance } X = \frac{\text{wt. of unit vol. of substance}}{\text{wt. of unit vol. of } X}.$$

The standard substance for solids and liquids is water at 4° C.; for gases

$$\text{Density to } \tfrac{1}{32} \text{ oxygen}^2 = \frac{\text{wt. of one liter of gas}}{\text{wt. of one liter of ideal gas, } \tfrac{1}{32}\ O_2\ (0.044656)},$$

$$\text{Density to air} = \frac{\text{wt. of one liter of the gas}}{\text{wt. of one liter of air } (1.2926)},$$

$$\text{Density to hydrogen} = \frac{\text{wt. of one liter of the gas}}{\text{wt. of one liter of hydrogen } (0.089873)};$$

hence it is evident that given the specific gravity (vapor density) of a gas to hydrogen, to obtain the molecular weight m, divide the weight w of a liter by 2.016, the molecular weight of hydrogen:

$$\frac{0.089873}{2.016} = 0.044580; \text{ therefore } m = \frac{w}{0.04450}.$$

Air weighs 1.2926 g. per liter under standard conditions; considering it to be a chemical compound it has a molecular weight referred to $\frac{1}{32}$ oxygen of

$$\frac{1.2926}{0.044656} = 28.946.$$

[1] When the metric system is employed, the specific gravity and the density of a gas is numerically the same if the unit of volume is the liter. As already mentioned, the terms relative density and specific gravity are synonymous; when dealing with gases the term vapor density is frequently employed.

[2] The specific gravity to $\frac{1}{32}$ oxygen is the molecular weight.

Consequently, given the specific gravity g of a gas referred to air, the molecular weight m is

$$m = g \times 28.946,$$

and, conversely, given the molecular weight, its specific gravity is

$$g = \frac{m}{28.946}.$$

The density of a gas (pressure remaining constant) is inversely proportional to the absolute temperature, that is,

$$\frac{D}{D'} = \frac{T'}{T};$$

also the density of a gas varies directly as the pressure (temperature remaining constant), or

$$\frac{D}{D'} = \frac{P}{P'}.$$

Graham's Law. — The volumes of two gases which diffuse in equal times under the same conditions are inversely proportional to the square roots of their densities. Effusion, or the passage of gases through a minute orifice in a thin plate, obeys the same law as diffusion, which is the passage of gases through a porous diaphragm. The analytical expression of this law is

$$\frac{V_1}{V_2} = \frac{\sqrt{D_2}}{\sqrt{D_1}}, \quad \text{or} \quad \frac{V_1^2}{V_2^2} = \frac{D_2}{D_1},$$

in which V_1 is the volume of a gas of density D_1 which diffuses or effuses in the same time as a volume V_2 of another gas of density D_2.

Bunsen found that the ratios of the times of diffusion (or effusion) of two gases which will diffuse (or effuse) the

same volume is directly proportional to the square roots of their densities; that is,

$$\frac{T_1}{T_2} = \frac{\sqrt{D_1}}{\sqrt{D_2}}, \quad \text{or} \quad \frac{T_1^2}{T_2^2} = \frac{D_1}{D_2},$$

in which D_1 is the density of a gas that requires time T_1 to diffuse (or effuse) the same volume as the gas of density D_2 which requires time T_2.

Volume Occupied by a Gram Molecule of a Gas. — A gram molecule of a substance will be defined as that weight of the substance, in grams, numerically equal to its molecular weight. For example, the molecular weight of oxygen is 32, hence a gram molecule of oxygen is 32 g. Given the following:

Substance.	Molecular weight.
(*a*) Cl_2	70.92
(*b*) HCl	36.468
(*c*) CO_2	44.00

to find the volume occupied by one gram molecule of each of these substances.

(*a*) $70.92 \times 0.044656 = 3.167$ g. per liter,

$$\frac{70.92}{3.167} = 22.393 \text{ liters per gram molecule;}$$

or in one expression

$$\frac{70.92}{70.92 \times 0.044656} = 22.393 \text{ liters per gram molecule.}$$

(*b*) Similarly,

$$\frac{36.468}{36.468 \times 0.044656} = 22.393 \text{ liters per gram molecule.}$$

(*c*) In the same way,

$$\frac{44.00}{44.00 \times 0.044656} = 22.393 \text{ liters per gram molecule.}$$

A consideration of Avogadro's law would have led to these results, for since all equal volumes of gases under the same conditions contain the same number of molecules, and as this fact serves as a means of determining molecular weights, it follows that if weights of gases are taken according to their molecular weights, these gases must occupy the same volume.

These facts give an alternative method for calculating the molecular weights of gases, being given the weight of a specified volume. As one gram molecule of a gas occupies 22.4 liters [1] at standard conditions of temperature and pressure, the molecular weight of a gas is that weight, in grams, which will occupy this volume. To calculate the molecular weight of propylene: 298.5 cc. of propylene at 18° C. and 768 mm. weigh 0.5315 g. Reducing this volume to 0° C. and 760 mm.,

$$\frac{273}{291} \times \frac{768}{760} \times 298.5 = 283 \text{ cc.}$$

Then, the molecular weight being the weight of 22.4 liters,

$$\frac{22{,}400}{283} \times 0.5315 = 42.07.$$

Measurement of Vapor Density. There are three general methods for obtaining vapor density. These are the methods of Dumas, Victor Meyer and Hofmann.

Dumas' Method is applicable to gases and liquids which may be vaporized. In this method, a bulb of about 200 cc. capacity is provided with a narrow neck through

[1] The law of Charles states that gases have the same coefficient of thermal expansion. This is not strictly true; although the coefficients are nearly equal, they differ to a slight extent. This being the case, all gases at 0° C. and 760 mm. will not occupy exactly the same volume. 22.4 liters may be taken as an approximate value in the majority of cases. This volume is termed the gram molecular volume (G.M.V.).

which the material is introduced and which is sealed when full of the gas to be determined. To make a vapor density determination, a small quantity of the liquid to be investigated is introduced or the gas is passed in, displacing the air, after ascertaining the weight of the open bulb in air. If used for a liquid the bulb is placed in a water or oil bath which is about 25° C. above the boiling point of the liquid introduced, which is thereby vaporized and escapes through the neck. As soon as no more vapor issues from the bulb, the neck is sealed off by a blowpipe and the temperature of the bath is taken. After cooling, the bulb is again weighed and then the neck is broken off under water, which is drawn into the flask, filling it completely, except for a small bubble. Filling the bulb and weighing the water it holds gives the capacity, the barometer reading giving the pressure of the gas. If D is the vapor density of the substance, W the weight of the vapor in the bulb at the temperature of the bath and at atmospheric pressure,[1] and W' the weight of the air which the bulb would hold at the same temperature, then the vapor density compared with air is

$$D = \frac{W}{W'}.$$

The Method of Victor Meyer is not applicable to gases, but only to substances which volatilize without decomposition, and consists in vaporizing a known weight of substance at a temperature considerably above its boiling point in an apparatus of special form. The vapor displaces its own volume of an inert gas, which is collected (usually over water) and its volume measured, noting the temperature and the height of the barometer.

[1] Correction should be made for the buoyant effect of weighing in air. This will be treated subsequently.

The volume of air is corrected to standard conditions, dry. Knowing the weight of substance taken and the volume which it occupies in the form of vapor, the vapor, the density, or what is more often required, the molecular weight, is easily calculated. Suppose 0.1910 g. of substance gave 60.50 cc. of air at 11° C. and 752 mm. To calculate the molecular weight (vapor density to $\frac{1}{32}$ oxygen). As the air was measured over water, the volume must be calculated to standard conditions, dry. The tension of aqueous vapor at 11° C. is 9.81 mm.

$$\frac{273}{284} \times \frac{752 - 9.81}{760} \times 60.50 = 56.79 \text{ cc.}$$

The weight of vapor which would be required to fill 22.4 liters (the molecular weight) is

$$\frac{22{,}400}{56.79} \times 0.1910 = 75.34.$$

Hofmann's Method is used for substances which may be volatilized undecomposed and consists in vaporizing a known weight of substance at a constant known temperature *in vacuo*. This is usually done over mercury. A graduated glass tube closed at one end is filled with mercury and inverted in a mercury trough. The height of the mercury is noted and a weighed amount of substance in a small bottle is introduced into the tube by inserting it under the mercury up into the open end of the tube. The tube is surrounded by a jacket through which circulates steam or vapor from some high boiling point substance. The temperature maintained in the jacket is considerably higher than the boiling point of the substance examined. This high temperature drives the stopper out of the bottle, vaporizes the substance and depresses the column of mercury, the height of which is

noted.[1] From the position of the mercury, the volume and the pressure of the vapor inside the tube is determined. The temperature of the vapor is read. This will be the temperature of the jacket. Suppose 0.0648 g. of substance yields 65.30 cc. of vapor at 100° C., the barometer reading 752 mm., the mercury in the tube standing 480 mm. above the level of the mercury in the trough. To calculate the molecular weight of this substance (neglecting corrections for the expansion of the mercury, its vapor tension and its specific gravity).

$$\frac{273}{373} \times \frac{752 - 480}{760} \times 65.30 = 17.11 \text{ cc. at } 0° \text{ C. and } 760 \text{ mm.}$$

The weight of 22.4 liters, or the molecular weight, is

$$\frac{22{,}400}{17.11} \times 0.0648 = 84.86.$$

Deviations from the Gas Laws. — Up to the present, calculations have been made assuming the absolute truth of the laws of Charles and Boyle. These laws are only approximations, for, as the critical points of a gas are approached or the gas is near a change of state, the laws lose accuracy. A gas far removed from its liquefaction point acts very closely in accordance with the laws of Charles and Boyle; the farther removed, the closer its compliance with these laws. It can only be said then, that if the gas under consideration acted as an ideal gas (an ideal gas is an imaginary gas which obeys the laws of Charles and Boyle) the predictions would be

[1] By this method, the gas may be obtained under reduced pressure, which may allow of the examination of substances which decompose on heating to their boiling point under higher pressures. Further, the diminishing of the pressure by lowering the boiling point allows of a lower temperature being employed for vaporization.

correct.[1] As an instance, carbon disulphide has a molecular weight of 76.12, while its specific gravity to $\frac{1}{32}$ oxygen is 76.4. The volume occupied by a gram molecule of this gas is

$$\frac{76.12}{76.4 \times 0.044656} = 22.31 \text{ liters.}$$

Also, mercuric chloride having a molecular weight of 271.52, in gaseous condition shows a specific gravity to $\frac{1}{32}$ oxygen of 283.5. The volume occupied by a gram molecule is then

$$\frac{271.52}{283.5 \times 0.044656} = 21.47 \text{ liters.}$$

This last case is a considerable divergence from the theoretical and it will be noted that in this case the volume of gas is taken of a substance which at ordinary temperatures is a solid. Water at 0° C. and 76 cm. pressure is ordinarily in the solid condition, but at elevated temperatures becomes gaseous. The same is true of mercury and other substances which at ordinary temperatures do not exist as gases. It may be predicted, however, that if they were in the gaseous state they would approximate the volume calculated from the gas equations. Thus, if steam, H_2O, with a molecular weight of 18.016 existed as a gas at 76 cm. and 0° C., one gram molecule would occupy 22.4 liters. Also, the molecular weight of mercury is 200.6 (the atom and the molecule of mercury are the same); then 200.6 g. of mercury vapor

[1] It is for this reason that some of the answers given to the problems do not agree exactly with data obtained from chemists' handbooks, it often happening that the specific gravity calculated and observed differ slightly. The reason for this is that molecular weights are often determined by gravimetric methods which in many cases are more accurate than those just described. See Chem. Ann., p. 3.

if it existed as a gas at standard conditions would occupy 22.4 liters. On this basis it is possible to calculate the volume of mercury vapor and the volume of any weight of it at any temperature at which it is a gas. One gram of mercury vapor at standard (if it were a gas) would occupy

$$\frac{1.000}{200.6} \times 22.4 = 0.1117 \text{ liters},$$

and at 400° C. the volume of this amount would be

$$\frac{673}{273} \times 0.1117 = 0.2753 \text{ liters},$$

and the volume of the vapor at one-half atmospheric pressure,

$$\frac{760}{380} \times 0.2753 = 0.5506 \text{ liters} = 550.6 \text{ cc}.$$

To restate the problem: What is the volume of 1.000 g. of mercury vapor at 400° C. and under one-half atmospheric pressure. Solving, by one expression,

$$\frac{1.000}{200.6} \times \frac{673}{273} \times \frac{760}{380} \times 22.4 = 0.5506 \text{ liters}.$$

This is a fair approximation to the truth, as the mercury would be in the vapor state, the boiling point of mercury under atmospheric pressure being 357.33° C.

Volume of Gas from Weight of Substance (in Metric System). — The foregoing yields a method for calculating the volumes of a gas resulting from a given weight of a reacting substance. Take the reaction:

	$2\,KClO_3$	$=$	$2\,KCl$	$+$	$3\,O_2$
(*a*) Parts by weight (g.)	2 (122.56)	=	2 (74.56)	+	3 (32)
(*b*) Parts by vol.[1]	2 vols.		2 vols.		3 vols.
					= 3 (22.4) liters.

[1] Potassium chlorate and potassium chloride are not gases, but if they were, the volume relations of (*b*) would hold if they corresponded to the formulas assigned to them.

Volume of Gas from Weight of Substance (in Ounces). — By a coincidence approximately the same relations exist between the volume of a gas in liters and its weight expressed in grams and the volume of a gas expressed in cubic feet and its weight expressed in ounces; for one cubic foot = 28.32 liters and one ounce = 28.35 g. For example, one gram molecule of oxygen has been shown to occupy 22.4 liters. To calculate how many cubic feet in 32 ounces of oxygen,

$$1 \text{ oz.} = 28.35 \text{ g.}, \; 1 \text{ cu. ft.} = 28.32 \text{ L.};$$

therefore

$$32 \text{ oz. will occupy } 22.4 \times 28.35 = 635.04 \text{ L.},$$

and

$$\frac{635.04}{28.32} = 22.42 \text{ cu. ft.}$$

Consequently, gas calculations being rough in most cases, it is possible to calculate chemical equations involving gases to units in the English system with the same facility as with the metric system. Defining an ounce molecule as that weight in ounces corresponding to the molecular weight, the volume of an ounce molecule of a gas under standard conditions is 22.4 cubic feet.[1]

Calculation of Weighings in Air to Values in Vacuo and Vice Versa. — The principle of Archimedes as stated is that a substance immersed in a liquid is buoyed up (loses weight) by an amount equal to the weight of the liquid displaced. If for the term "liquid," the term "fluid" is substituted, the law has a more general application, for gases come under the head of fluids.

Commonly, weighings are carried out in the atmosphere; consequently, the weight of an object shown by the ordi-

[1] If the English system is used in all the units, it is better to calculate the temperature to Absolute. The other units, such as inches of mercury, may be retained.

nary balance may not be the true weight, as the object weighed has displaced a certain amount of air, and consequently has lost weight by an amount equal to the weight of the air displaced. If, however, the weights used to counterbalance the object are of the same volume they have likewise lost weight to the same extent; consequently, the mass shown by the counterpoising weights is the true mass of the object weighed. If, on the other hand, the substance weighed and the weights used to counterpoise are of different volumes, the mass may be more or less than the true weight. If the volume of the substance is greater than that of the weights counterbalancing it, the substance has lost weight, and the apparent value is smaller than the real value; if the weights occupy a greater volume than the object weighed they have lost weight to a greater extent than the object and the apparent weight of the object is larger than the real value. Let W be the true weight *in vacuo* of the body of a density D. The body then occupies a volume $\frac{W}{D}$. Let W' be the apparent weight of the standard grams necessary for counterpoise and D' the density of the standard grams. The volume of the standard grams is $\frac{W'}{D'}$. If d be the weight of a unit volume of air at the time of weighing, then the weights have lost $\frac{W'}{D'}d$ and the loss of weight of the object is $\frac{W}{D}d$. Then the condition of equilibrium is

$$W - \frac{W}{D}d = W' - \frac{W'}{D'}d.$$

[1] The weights are supposed to be corrected so that *in vacuo* they have this value.

Solving for W and W' gives

$$W = W' + d\left(\frac{W'}{D'} - \frac{W}{D}\right); \; W' = W + d\left(\frac{W}{D} - \frac{W'}{D'}\right);$$

also

$$W = W' \frac{1 - \frac{d}{D'}}{1 - \frac{d}{D}}; \; W' = W \frac{1 - \frac{d}{D}}{1 - \frac{d}{D'}};$$

and since d is small in comparison with D and D', by division the above expressions give

$$W = W' + W'd\left(\frac{1}{D} - \frac{1}{D'}\right); \; W' = W + Wd\left(\frac{1}{D'} - \frac{1}{D}\right).$$

The latter form is more convenient for general use as $W'd\left(\frac{1}{D} - \frac{1}{D'}\right)$, or $Wd\left(\frac{1}{D'} - \frac{1}{D}\right)$ may be solved once for all and tabulated for bodies of differing densities as brass weights are almost universally used.[1]

Standard (United States) Unit of Volumetric Apparatus. — The metric system was designed to connect the units of length and mass. The gram was intended to be the mass of a cube of water, at 4° C., of one centimeter edge. Or, the kilogram was to be the mass of a cube of water, at 4° C., of one decimeter edge. This relationship was very closely approximated, but the error is appreciable, a kilogram of water being found to contain 1000.027 cc. This discrepancy is very small and causes no inconvenience, but because of it, the units of capacity for volumetric apparatus have been changed. The liter, defined as the volume occupied by a quantity of pure water at 4° C., having a mass of one kilogram, and the one-thousandth part of the liter, called the milliliter

[1] See Stewart and Gee, "Elementary Practical Physics," Vol. 1, p. 90; also Treadwell, "Analytical Chemistry," Vol. 11, p. 14, 1912.

or cubic centimeter, are employed as units of capacity.[1] As 4° C. is an inconvenient temperature to work at, volumetric apparatus is calibrated to contain, or deliver, a specified volume at some other temperature. In this country 20° C. has been adopted by the Bureau of Standards. At whatever temperature the apparatus is calibrated to contain or deliver, this temperature should be marked on the instrument.

Volumetric instruments are often calibrated by weighing into them the calculated amount of water at a definite temperature which the instrument should contain, or deliver, to be correct. As the weighing is done in air, correction must be made for the buoyant effect of air. The water to be weighed may or may not be at the temperature at which the instrument is calibrated to be correct, and allowance must be made for the expansion of the water and the glass. The cubical coefficient of expansion of the glass in volumetric apparatus is taken as 0.000025 for each degree centigrade. Suppose the temperature at which the instrument is calibrated to be correct is 20° C., the expression for the volume of water the instrument is to contain, or deliver, at other temperatures is

$$V = v + v \times 0.000025\,(20 - t°),$$

in which V is the volume at 20° C., v the volume at $t°$ C., the temperature ($t°$) at which the water and the instrument are at the time of calibrating.

Thus, to calculate the weight, W', of water, which should be weighed into a flask at $t°$ C. such that the meniscus shall be at the place to be marked to show a correct volume at 20° C. Let V be the volume it is desired to have the flask contain at 20° C. and d the density of the water

[1] Circular of the Bureau of Standards, No. 9; also Sutton, Volumetric Analysis, p. 24, 1911.

at $t°$ C. Let b be the buoyancy constant,[1] t the temperature of the flask and water at the time of weighing. Then the number of grams W', which should be placed on the other pan (the flask being tared by a similar flask and beads, foil, etc.), is

$$W' = Vd + Vbd + V \times 0.000025\,(20 - t),$$

in which d is the density of water at the temperature t.

The Mohr Liter. — Mohr proposed as a unit of volume that volume occupied by one gram of water at 17.5° C. weighed in air with brass weights. In English-speaking countries 60° F. or 15.5° C. is commonly used as also is 15° C. In standard flasks, burettes, etc., the temperature at which it was calibrated is always marked on standard instruments.[2] To calculate, for example, the true capacity of a Mohr's cubic centimeter:

Air at standard weighs 0.0012926 g. per cc.; then at 17.5° C., the barometer being at standard:

[1] The buoyancy constant for a body of a specified specific gravity is obtained by solving $d\left(\frac{1}{D} - \frac{1}{D'}\right)$ for correcting weighings made in air to obtain values *in vacuo* and conversely $d\left(\frac{1}{D'} - \frac{1}{D}\right)$ for converting weights *in vacuo* to weights in air. This latter quantity is intended as the value of (b) in the above.

[2] "Measures marked, *e.g.*, '25 cc. 15° C.' should contain or deliver, as the case may be, 25 true cc. when the instrument is at the temperature of 15° C. On the other hand, a flask marked '1000 g. 16° C.' should, of course, contain 1000 g. of distilled water at the temperature of 16° C., *i.e.*, a Mohr's liter. Vessels graduated according to Mohr's system should bear the word 'gramme' or the letters 'grm' together with the temperature. It should be noted that the German Kaiserliche Normal-Eichungs Kommission no longer employs Mohr's unit." Sutton, Volumetric Analysis, p. 24. As to the last sentence, the United States Bureau of Standards could also be included.

$$\frac{1}{1 + 0.00367 \times 17.5} \times 0.0012926 = 0.0012146 \text{ g. per cc.}$$

One gram of water at 17.5° C. = 1.001289 cc., then $1.001289 \times 0.0012146 = 0.0012162$ g. air displaced by the water.

$\frac{1}{8.4} = 0.11905$ cc. air displaced by the weights.

$0.11905 \times 0.0012146 = 0.0001446$ g. air displaced by the weights.

$0.0012162 - 0.0001446 = 0.0010716$ g. loss of weight of the water.

$1.0000000 + 0.0010716 = 1.0010716$ g. true weight of 1 cc. of water under these conditions equals 1.001072 true cc.

$1.001289 - 1.000000 = 0.001289$ cc. expansion of the water due to change from 4° C. to 17.5° C.

$1.001072 + 0.001289 = 1.00236$ true cc. in a cubic centimeter as recommended by Mohr. Then a Mohr's liter is 1002.36 true cc., or is 2.36 cc. larger than a true liter.

Dalton's Law of Partial Pressures. — The pressure exerted by a mixture of gases, or of gases and vapors, or vapors, which do not react chemically, is equal to the sum of the pressures which each would exert if it alone occupied the whole space occupied by the mixture. For simplicity a gas saturated with water vapor will be considered. Let

P_g° = pressure of a dry gas corresponding to a volume V_g° and a temperature T°,

P_g' = pressure of the same gas corresponding to a volume V_g' and a temperature T'.

By the laws of Boyle and Charles:

$$\frac{V_g^\circ}{V_g'} = \frac{P_g'}{P_g^\circ} \times \frac{T^\circ}{T'}. \qquad (1)$$

Let this gas be at V_g', P_g' and T' and let it be saturated with water vapor. Let

V'_{g+w} = volume of the mixture after saturation,
P'_{g+w} = pressure of the gas after saturation,
P'_w = pressure of aqueous vapor at T'.

Then, by Dalton's law,

$$P'_{g+w} = P'_g + P'_w; \text{ whence } P'_g = P'_{g+w} - P'_w.$$

Substituting in (1)

$$\frac{V_g^\circ}{V'_{g+w}} = \frac{P'_{g+w} - P'_w}{P_g^\circ} \times \frac{T^\circ}{T'}. \qquad (2)$$

Now let the gas be at P_g°, V_g° and T°, and let it be saturated with water vapor. Let

V°_{g+w} = volume of the mixture after saturation,
P°_{g+w} = pressure of the gas after saturation,
P_w° = pressure of aqueous vapor at T°.

Then, as before,

$$P^\circ_{g+w} = P_g^\circ + P_w^\circ; \text{ whence } P_g^\circ = P^\circ_{g+w} - P_w^\circ.$$

Substituting these values in (2)

$$\frac{V^\circ_{g+w}}{V'_{g+w}} = \frac{P'_{g+w} - P_w'}{P^\circ_{g+w} - P_w^\circ} \times \frac{T^\circ}{T'}.^1$$

The weight of a moist gas is the weight of the dry gas plus the weight of the water vapor. Let

W_{g+w} = weight of V_g° volumes of moist gas at a pressure P°_{g+w} and a temperature T°,
W_g = weight of V_g° volumes of dry gas at a pressure P_g° and a temperature T°,

[1] The discussion given on page 85, correcting the volume of a moist gas to the volume which the gas would occupy if dry, is a single case of Dalton's law. For values of the tension of aqueous vapor, see Chem. Ann., pp. 461–466. Mercury also has a small vapor pression; see Chem. Ann., p. 468.

W_w = weight of $V_g°$ volumes of water vapor at a pressure $P_w°$ and a temperature $T°$,

A = weight of a unit volume of dry gas at $P_g°$ and $T°$,

B = weight of a unit volume of water vapor at $P_g°$ and $T°$.

Then

$$W_g = \frac{P'_{g+w} - P_w'}{P_g°} \times \frac{T°}{T'} \times A.$$

Since the weight of a gas is directly proportional to its pressure and inversely proportional to its temperature, and

$$W_w = \frac{P_w'}{P_g°} \times \frac{T°}{T'} \times B,$$

then

$$W_{g+w} = W_g + W_w.$$

For similar reasons

$$W_{g+w} = \frac{P'_{g+w} - P_w'}{P_g°} \times \frac{T°}{T'} \times A + \frac{P_w'}{P_g°} \times \frac{T°}{T'} \times B.$$

By means of this formula, the weight of a moist gas may be calculated for any temperature and pressure. For a specified gas, the formula may be considerably shortened. Take, for example, air saturated with water vapor. The density of aqueous vapor compared to air is

$$\frac{18.016}{28.943} = 0.62247 = \frac{5}{8}, \text{ approximately.}$$

Let

A = weight of a unit volume of dry air at $P_g°$ and $T°$,

B = weight of a unit volume of water vapor at $P_g°$ and $T°$,

W_{a+w} = weight of a unit volume of saturated air at $P_g°$ and $T°$.

Then

$$B = \tfrac{5}{8} A.$$

Then the weight of a unit volume of saturated air at P' and T' is

$$W_{a+w} = \frac{P'_{g+w} - P_w'}{P_g^\circ} \times \frac{T^\circ}{T'} \times A + \frac{P_w'}{P_g'} \times \frac{T^\circ}{T'} \times \tfrac{5}{8} A,$$

$$W_{a+w} = \frac{P'_{g+w} - \frac{3}{8} P_w'}{P_g^\circ} \times \frac{T^\circ}{T'} \times A.$$

But as the weight of a liter of air is given at 0° C. and 760 mm., then

$$P_g^\circ = 760,\ T^\circ = 273 \text{ and } A = 1.2926 \text{ g.}$$

Substituting,

$$W_{a+w} = \frac{P'_{g+w} - \frac{3}{8} P_w'}{760} \times \frac{273}{T'} \times 1.2926.^1$$

Use of this formula is as follows: It is desired to know the weight W_{a+w} of a liter of air saturated with moisture at 15° C. (T') under a pressure of 754 mm. (P'_{g+w}). The weight of a liter of a gas is given under standard conditions, *i.e.*, temperature 273° A., and pressure 760 mm. Of air this weight is 1.2926 g. The tension of aqueous vapor P_w' at 15° C. is 12.76 mm.[2] Substituting in the formula,

$$W = \frac{273}{288} \times \frac{754 - \frac{3}{8} 12.76}{760} \times 1.2926 = 1.2078 \text{ g.}$$

[1] The fraction $\frac{3}{8}$ is applicable only to air. For any other gas the requisite fraction could be worked out in the same manner as given for air.

[2] The value 12.76 mm. is given to this degree of accuracy in the tables. When subtracted from the barometric reading given in millimeters, the result would give a reading which is apparently accurate to hundredths of a millimeter, and to be significant, would require that the barometric reading was accurate to hundredths of a millimeter, which is seldom the case. In the solution of problems, however, the vapor pressures have been subtracted from the barometric readings as if these were as accurate as the tabulated values of the vapor pressures.

Again, it is required to find the weight of dry oxygen contained in a liter of oxygen saturated with moisture at 17° C. and under a pressure of 750 mm. (ten. aq. vap. at 17° C. = 14.45 mm.).

$$W' = \frac{273}{290} \times \frac{750 - 14.45}{760} \times 32 \times 0.044656 = 1.3019 \text{ g. } O_2,$$

$$W'' = \frac{273}{290} \times \frac{14.45}{760} \times 18.016 \times 0.044656$$

$$= 0.0144 \text{ g. } H_2O \text{ vapor},$$

$$W = 1.3019 + 0.0144 = 1.3163 \text{ g.}$$

A gas need not be saturated; a knowledge of the degree of saturation will suffice, from which the tension of the aqueous vapor may be calculated. In the case of moisture present in the atmosphere this may be readily determined by taking the dew point. The dew point is that temperature at which the air would be saturated if it contained the amount of water which is present at the time and place of determination. For example, it is necessary to know the aqueous pressure exerted in the laboratory at a certain time. Suppose the dew point is found to be 15° C. On consulting the table of aqueous tensions [1] the tension of aqueous vapor at 15° C. is found to be 12.73 mm. The relative humidity is the ratio between the amount of aqueous vapor present in the air at a certain time and place, and the amount which would need to be present to saturate the air at the temperature of the air at the time of taking. As an example: The dew point at a certain time and place was found to be 10° C. The temperature of the atmosphere was 20° C. The tension of saturated aqueous vapor at 10° C. is 9.18 mm.; at 20° C. it is 17.41 mm.; then the relative humidity is

$$\frac{9.18}{17.41} = 0.5273 = 53\%.$$

[1] See Chem. Ann., pp. 461–467.

PROBLEMS

I. 200 cc. of a gas are at a pressure of 752 mm.[1] and 15° C.: (*a*) What is the volume under a pressure of 770 mm., temperature remaining constant? (*b*) What is the volume if the temperature is lowered to 10° C., pressure remaining constant? (*c*) What is the volume if changed from 752 mm. and 15° C. to 770 mm. and 10° C.?

Ans.

(*a*) $\frac{752}{770} \times 200 = 195.33$ cc.

(*b*) 15° C. = 273 + 15 = 288° A.; 10° C. = 273 + 10 = 283° A.

$$\frac{283}{288} \times 200 = 196.53 \text{ cc.}$$

(*c*) $\frac{283}{288} \times \frac{752}{770} \times 200 = 191.94$ cc.

II. A barometer graduated on a glass scale reads 763.4 mm. at 19.5° C. (*a*) What is the reading corrected to 0° C.? (*b*) If the corrected height of a barometer with a brass scale is 764.7 mm., what does the barometer read at 22° C.? (*c*) If a barometer with a glass scale reads 754.3 mm. at − 10 C°., what is the height corrected to standard?

Ans. (*a*) $\frac{763.4}{1 + 19.5 \times 0.00017} = \frac{763.4}{1.003315} = 760.9$ mm.

(*b*) $\frac{X}{1 + 22 \times 0.00016} = 764.7.$

$$X = 764.7 \times (1 + 22 \times 0.00016) = 767.39 \text{ mm.}$$

(*c*) $\frac{754.3}{1 - 10 \times 0.00017} = 755.6$ mm.

[1] Unless otherwise stated, barometer readings in all problems are supposed to be corrected to values at 0° C. Barometer readings will be supposed to be correct as far as the second place past the decimal point even if given only to the decimal point. Thermometer readings will be considered correct to the second decimal place.

III. A gas at 750 mm. and 12° C., measured moist, has a volume of 325 cc. (*a*) What is its volume, dry, under the same conditions? (*b*) Dry, at standard? (*c*) 160 cc. of a gas are measured moist at 15° C., the barometer (corrected) reads 743 mm. The mercury in the tube stands 150 mm. above the trough; what is the volume of the gas, dry, at standard?

Ans.

(*a*) Tension of aqueous vapor at 12° C. = 10.48 mm.

$$\frac{750 - 10.48}{750} \times 325 = \frac{739.52}{750} \times 325 = 320.46 \text{ cc.}$$

(*b*) $$\frac{750 - 10.48}{760} \times \frac{273}{285} \times 325 = 302.93 \text{ cc.}$$

(*c*) Tension of aqueous vapor at 15° C. = 12.73 mm. Using the decimal coefficient for the change of volume due to change in temperature,[1]

$$\frac{743 - (150 + 12.73)}{760} \times \frac{1}{1 + 0.00367 \times 15} \times 160 = 115.8 \text{ cc.}$$

IV. How many cubic centimeters of nitrogen gas, at standard, can be obtained from a liter of ammonia gas, at 15° C. and 780 mm.?

Ans.

$$\underset{\text{2 vol.}}{2\,NH_3} = \underset{\text{1 vol.}}{N_2} + \underset{\text{3 vol.}}{3\,H_2},$$

$$\frac{1}{2} \times \frac{273}{288} \times \frac{780}{760} \times 1000 = 486.43 \text{ cc.}$$

V. A gaseous mixture contains nitrous oxide (N_2O), nitric oxide (NO) and nitrogen. Calculate the composition of the mixture from the following:

Volume of mixture taken	51.00 cc.
Volume after adding hydrogen	108.30 cc.

[1] Where considerable accuracy is desired, the particular decimal coefficient of expansion of the gas under consideration should be used. See Chem. Ann., p. 73. Unless otherwise stated, the factor used in obtaining the answers to problems will be $\frac{1}{273}$.

Volume after explosion	51.00 cc.
Volume after adding oxygen	76.50 cc.
Volume after explosion	57.60 cc.

Ans. Let x = cc. N_2O,
y = cc. NO,
z = cc. N_2.
H_2 added = 108.3 − 51.00 = 57.30 cc.
Contraction = 76.50 − 57.60 = 18.90 cc.
$\frac{2}{3} \times 18.90 = 12.60$ cc, H_2 added in excess.

57.30 − 12.60 = 44.70 cc. is the required amount of H_2 necessary for the first explosion. The reactions are:

$$N_2O + H_2 = N_2 + H_2O,$$
$$x + x = x + 0$$
$$2\,NO + H_2 = N_2 + H_2O,$$
$$2y + y = y + 0.$$

Then the contraction due to the H_2 explosion is

(1) $$x + y = 44.70 \text{ cc.}$$

After the first explosion, if no H_2 had been added in excess, the volume would be z cc. N_2 originally present, x cc. N_2 from the N_2O, and $\frac{y}{2}$ cc. of N_2 from the NO; this is 51.00 − 12.60 = 38.40 cc. Hence

(2) $$x + \frac{y}{2} + z = 38.40 \text{ cc.}$$

Then

(3)	$x + y + z = 51.00$ cc.	(2)	$2x + y + 2z = 76.80$ cc.
(2)	$2x + y + 2z = 76.80$ cc.	(1)	$x + y = 44.70$ cc.
(4)	$x + z = 25.80$ cc.		$x + 2z = 32.10$ cc.
		(4)	$x + z = 25.80$ cc.
			$z = 6.30$ cc.

Substituting in (4) gives $x = 19.50$ cc.
Substituting these values in (3) gives $y = 25.20$ cc.

VI. (*a*) A liter of sulphur dioxide at standard weighs 2.9266 g. Calculate its molecular weight. (*b*) The molecular weight of

acetylene is 26.016; what is the weight of 250 cc. of the gas at 18° C. and 757 mm.? (*c*) If the specific gravity of hydrogen selenide referred to air is 2.806, what is its weight per liter? (*d*) Its molecular weight?

Ans.

(*a*) $\frac{2.9266}{0.044656} = 65.5$; also, $2.9266 \times 22.393 = 65.5$.

(*b*) $26.016 \times 0.044656 = 1.1617$ g. per L. at standard,

$\frac{273}{291} \times 1.1617 = 1.0899$ g. per L. at 18° C. and 760 mm.

$\frac{757}{760} \times 1.0899 = 1.0856$ g. per L. at 18° C. and 757 mm.

$\frac{250}{1000} \times 1.0856 = 0.2714$ g. in 250 cc. at 18° C. and 757 mm.

or in one expression,

$$26.016 \times 0.044656 \times \frac{273}{291} \times \frac{757}{760} \times \frac{250}{1000} = 0.2714 \text{ g.}$$

(*c*) $2.806 \times 1.2926 = 3.627$ g. per L.

(*d*) $2.806 \times 28.943 = 81.21$.

VII. (*a*) If 30.82 cc. of oxygen (density to air, 1.1055) effuses through a small orifice in 55 seconds, what volume of hydrogen (density to air, 0.06965) will effuse in the same time under the same conditions? (*b*) What volume of sulphur dioxide will effuse through a small orifice in the same time as 83 cc. of ammonia? (*c*) 150 cc. of air effuses in the same time as 63.82 cc. of bromine. What is the molecular weight of the bromine?

Ans.

(*a*) Substituting in the formula, $V_1 = \sqrt{\frac{V_2^2 D_2}{D_1}}$.

$$V_1 = \sqrt{\frac{(30.82)^2 \times 1.1055}{0.06965}} = 122.79 \text{ cc.}$$

(*b*) The densities of sulphur dioxide and ammonia are in the ratio of their molecular weights; then, as before,

$$V_1 = \sqrt{\frac{(83)^2 \times 17.034}{64.06}} = 42.80 \text{ cc.}$$

(*c*) Substituting in the proper formula:

$$D_2 = \frac{(150)^2 \times 1}{(63.82)^2} = 5.525, \text{ density to air,}$$

$$5.525 \times 28.943 = 159.89.$$

VIII. (*a*) What volume of oxygen at 18° C. and 754 mm. is liberated by 1.763 g. of potassium chlorate when completely decomposed? (*b*) How much sulphuric acid must be taken to obtain 5.5 cubic feet of hydrogen at 17° C. and 762 mm. by acting on a metal?

Ans. (*a*) $\underset{2\,(122.56)\text{ g.}}{2\,KClO_3} = 2\,KCl + \underset{3\,(22.4)\text{ L.}}{3\,O_2},$

$$\frac{1.763}{2\,(122.56)} \times \frac{291}{273} \times \frac{760}{754} \times 3\,(22.4) = 0.5193 \text{ L.}$$

(*b*) $\underset{98.09\text{ oz.}}{H_2SO_4} + M'' = M''SO_4 + \underset{22.4\text{ cu. ft.}}{H_2}$

$$\frac{5.5}{22.4} \times \frac{273}{290} \times \frac{762}{760} \times 98.09 = 22.73 \text{ oz.} = 1.42 \text{ lbs.}$$

IX. (*a*) A mass of aluminum (density, 2.583) weighed in air at 18° C. and 742 mm. showed an apparent weight of 149.2350 g., brass weights (density, 8.4) being used. What is its weight *in vacuo*? (*b*) A mass of platinum (density, 21.48) weighed in air at 15° C. and 765 mm., against brass weights, showed an apparent weight of 89.4130 g. Find its weight *in vacuo*.

Ans.

(*a*) $\frac{149.2350}{2.583} \times \frac{273}{291} \times \frac{742}{760} \times 0.0012926$

$= 0.0684$ g. lost by aluminum.

$$\frac{149.2350}{8.4} \times \frac{273}{291} \times \frac{742}{760} \times 0.0012926$$

$$= 0.0210 \text{ g. lost by weights.}$$

$0.0684 - 0.0210 = 0.0474$ g. difference in weights of air displaced.

$149.2350 + 0.0740 = 149.2824$ g., weight *in vacuo*.

(*b*) Using the formula $W = W' + W'd\left(\frac{1}{D} - \frac{1}{D'}\right)$,

$$d = \frac{273}{288} \times \frac{765}{760} \times 0.0012926 = 0.0012333,$$

$$W = 89.4130 + 89.4130 \times 0.0012333\left(\frac{1}{21.48} - \frac{1}{8.4}\right),$$

$$= 89.4130 + 89.4130 \times 0.0012333\ (0.04656 - 0.11905),$$

$$= 89.4130 + 89.4130 \times 0.0012333\ (-0.07249),$$

$$= 89.4130 - 0.0080 = 89.4050 \text{ g. } \textit{in vacuo}.$$

X. A flask which is to be marked to contain one liter at 20° C. (United States Standard) is counterpoised on a balance with a similar flask, finishing the counterpoising with sand foil, etc. How many grams of water must be weighed into it to give the position on the neck which should be marked? The conditions are:

Temperature of air in the balance	22° C.
Temperature of the water to be used	22° C.
Temperature of the flask	22° C.
Barometric pressure	765 mm.
Saturation of air in the balance	50%
Vapor pressure of water at 22° C.	19.66 mm.
Weight of a liter of dry air at 0° C. and 760 mm.	1.2926 g.
Coefficient of expansion of air	0.00367
Density of weights	8.4
Density of water at 20° C.	0.997797
Cubical coefficient of expansion of the glass	0.000025

Ans.

Weight of one cubic centimeter of air under these conditions is

$$\frac{1}{1 + (22 \times 0.00367)} \times \frac{765 - 0.50 \times \frac{3}{8} \times 19.66}{760}$$

$$\times 0.0012926 = 0.0011981 \text{ g.}$$

The weight of one liter of water in air under these conditions is:

$$W' = 1000 \times 0.997797 + 1000 \times 0.997797 \times 0.0011981\left(\frac{1}{8.4} - \frac{1}{0.997797}\right),$$

$$= 997.797 + 997.797 \times 0.0011981 \times (-0.883159)$$
$$= 997.797 - 1.056,$$
$$= 996.741 \text{ g.}$$

Correcting for the expansion of the glass gives

$$1000 \times 0.000025\,(20 - 22) = -0.05;$$

and the amount to weigh in is

$$996.74 - 0.05 = 996.69 \text{ g.}$$

137. One liter of a gas is under a pressure of 780 mm. What will be its volume at standard pressure (760 mm.), the temperature remaining constant? *Ans.* 1026.3 cc.

138. A gas of 300 cc. is under standard pressure. What will be its volume at 784 mm., the temperature remaining constant? *Ans.* 290.8 cc.

139. Five cubic feet of a gas are under a pressure of 27.3″ of mercury. What is its volume at 29.9″, the temperature remaining constant? *Ans.* 4.565 cu. ft.

140. A gas occupies a volume of 450 cc. under a pressure of 780 mm. The temperature remaining constant, what pressure must be applied to reduce the volume to 400 cc.? *Ans.* 877.5 mm.

141. A gas occupying a volume of one liter, under standard pressure, is expanded to 1200 cc. The temperature remaining constant, by how many millimeters must the pressure have been diminished? *Ans.* 126.7 mm.

142. A gas of 200 cc. is at 15.7° C. Find its volume at 0° C. (at standard), the pressure remaining constant? *Ans.* 189.12 cc.

143. One liter of a gas is measured at −15° C. What is its volume at 15° C., the pressure remaining constant? *Ans.* 1116.3 cc.

144. A gas measured 150 cc., at 17.5° C., and on account of a change in temperature, the pressure remaining constant, the volume decreased to 125 cc. What is the new temperature?

Ans. − 30.9° C.

145. The pressure on a confined gas, at 15° C., was 792 mm. If the pressure later registered 820 mm., what is the temperature then, the volume remaining unchanged? *Ans.* 25.17° C.

146. A liter of gas at standard conditions has its temperature raised to 15° C. What must be the pressure on the gas, if the volume of gas is unaltered? *Ans.* 801.7 mm.

147. 183 cc. of a gas are at standard; the pressure is then raised to 792 mm. What is the temperature, the volume remaining constant? *Ans.* 11.5° C.

148. 250 cc. of a gas are at a temperature of 15° C. What is the volume of the gas at 0° C., the pressure remaining constant? *Ans.* 237 cc.

149. The pressure on a certain volume of hydrogen is 730 mm. at the temperature of melting ice. The volume remaining constant, what is the temperature at a pressure of 750 mm.?

Ans. 7.48° C.

150. Given 250 cc. of a gas under a pressure of 765 mm. and at a temperature of 15° C., what is the volume corrected to standard conditions (0° C. and 760 mm.)? *Ans.* 238.5 cc.

151. A gas measures 300 cc. at standard conditions. What is its volume at 755 mm. and 17.5° C.? *Ans.* 321.3 cc.

152. Under standard conditions of temperature and pressure, a gas measures one liter. What is its volume at 17.7° C. and 748 mm.? *Ans.* 1082 cc.

153. A gas of 275 cc. under standard conditions changes its volume to 300 cc., when it is under a pressure of 754 mm. What is its temperature? *Ans.* 22.47° C.

154. 50 cc. of a gas at 780 mm. and at 10° C. changes its volume to 48 cc. under a pressure of 792 mm. What is the temperature at this pressure and volume? *Ans.* 2.87° C.

155. A gas is at a pressure of 748 mm. and a temperature of 12° C., when its volume is 200 cc. What must be the pressure of the gas if its volume is 178 cc., at a temperature of 0° C.?

Ans. 805.1 mm.

156. A volume of gas is confined at 0° C. and 760 mm. pressure. (*a*) What is this pressure in inches of mercury and (*b*) in pounds per square inch? (Sp. gr. of Hg = 13.6; 1″ = 2.54 cm.; 1 sq. in. = 6.4516 sq. cm.) *Ans.* (*a*) 29.92″.

(*b*) 14.701 lbs. per sq. in.

157. A barometer with a glass scale reads 752.6 mm. at 15° C. What is the barometer reading corrected to 0° C.?

Ans. 750.68 mm.

158. A barometer with a brass scale shows a pressure 768.5 mm. at 18° C. What is the barometer reading corrected to 0° C.? *Ans.* 766.28 mm.

159. The reading of a barometer, with a glass scale, at −5° C. is 753.2 mm. What is the reading corrected to 0° C.?

Ans. 753.84 mm.

160. A brass scale barometer reads 769.2 mm. at 15° F. What is the reading corrected to 0° C.? *Ans.* 770.36 mm.

161. What must be the reading on a barometer with a glass scale, at 15° C., that the pressure at 0° C. may indicate 760 mm.?

Ans. 761.9 mm.

162. If sufficient water is placed in a dry gas, at 15° C. and 753.8 mm. to thoroughly saturate it, what would be the pressure after saturation, the temperature remaining constant? (Ten. aq. vap. at 15° C. = 12.73 mm.) *Ans.* 766.53 mm.

163. If the atmosphere is saturated with water vapor at 14° C. and 758 mm., what percentage, by volume, of water vapor does it contain? (Ten. aq. vap. at 14° C. = 11.94 mm.)

Ans. 1.58%.

164. A gas, measured moist, has a volume of one liter at 17.5° C., under a pressure of 758.9 mm. What is its volume, dry, under standard conditions? (Ten. aq. vap. at 17.5° C. = 14.91 mm.) *Ans.* 919.9 cc.

165. 300 cc. of a gas are measured moist over water at 15° C. and under a pressure of 765 mm. (*a*) What would be its volume, dry, at this temperature? (*b*) What is its volume, dry, under standard conditions? (Ten. aq. vap. at 15° C. = 15.38 mm.) *Ans.* (*a*) 295.01 cc.
(*b*) 281.48 cc.

166. A certain reaction produces 22.4 L. of a gas, measured at standard conditions. (*a*) What volume would it occupy, moist, at 18° C. and at standard pressure? (*b*) At 18° C. and 770 mm.? (Ten. aq. vap. at 18° C. = 15.38 mm.)
Ans. (*a*) 24.36 L.
(*b*) 24.04 L.

167. 500 cc. of nitrogen are measured over water at 17° C., the barometer reading 750 mm. If the water stood 180 mm. in the tube, what is the volume of the nitrogen, dry, at standard? (Ten. aq. vap. at 17° C. = 14.91 mm.; sp. gr. Hg = 13.6.)
Ans. 447.07 cc.

168. 180.5 cc. of air, saturated with moisture, at 18° C., are measured over mercury, the barometer reading 620.3 mm. The mercury stood 52 mm. in the tube. Find the volume of the air, dry, at standard conditions. (Ten. aq. vap. at 18° C. = 15.38 mm.) *Ans.* 123.7 cc.

169. 203 cc. of chlorine gas, at standard conditions, are necessary to decompose a certain amount of hydrobromic acid gas, also at standard conditions. What is the volume of hydrobromic acid gas? *Ans.* 406 cc.

170. If to a mixture of 100 cc. of nitrogen and of 200 cc. of oxygen, 500 cc. of hydrogen are added, and the mixture exploded: (*a*) What is the resultant volume if the water is allowed to condense? (*b*) What is the resultant volume if the water stays in the gaseous state? *Ans.* (*a*) 200 cc.
(*b*) 600 cc.

171. Consider the following reactions:

(1) $2\,HBr + Cl_2 = 2\,HCl + Br_2$,
(2) $4\,HBr + O_2 = 2\,H_2O + 2\,Br_2$.

(*a*) If the volume of hydrobromic acid of (1) is one liter, how many liters of chlorine at the same conditions are necessary to liberate all the bromine? (*b*) In equation (2) how many volumes of oxygen of the same temperature and pressure are called for to liberate all the bromine? *Ans.* (*a*) 0.5 L.
(*b*) 0.25 L.

172. (*a*) How many cubic centimeters of nitrogen are contained in a liter of ammonia gas? (*b*) How many cubic centimeters of hydrogen? *Ans.* (*a*) 500 cc.
(*b*) 1500 cc.

173. One liter of hydrogen and 400 cc. of oxygen at 760 mm. and 15° C. are exploded in a confined space. What is the volume of the resultant gas at 170° C. and 760 mm. pressure?
Ans. 1538.2 cc.

174. What is the ratio of the volumes of hydrogen to chlorine involved when hydrochloric acid is formed? (*b*) The ratio of the volume of chlorine to the volume of hydrochloric acid produced? (*c*) What is the ratio of the sum of the initial volumes (factors) to the resultant volume (products)?
Ans. (*a*) 1/1.
(*b*) 1/2.
(*c*) 1/1.

175. One volume of ammonia gas is decomposed into its elements. (*a*) What is the volume of the resultant gases? (*b*) What is the ratio of the volume of the ammonia gas decomposed to the volume of the nitrogen produced? (*c*) What is the ratio of the volume of the nitrogen to hydrogen produced?
Ans. (*a*) 2 V.
(*b*) 2/1.
(*c*) 1/3.

176. 1200 cc. of chlorine and 1500 cc. of hydrogen at the same temperature and pressure are combined to form hydrochloric acid gas. (*a*) What volume of hydrochloric acid gas is formed? (*b*) Which gas is in excess and by how many cubic

centimeters? (*c*) What is the total volume of the gases after explosion? *Ans.* (*a*) 2400 cc.
(*b*) 300 cc. H_2.
(*c*) 2700 cc.

177. Assuming air to be $\frac{1}{5}$ oxygen: (*a*) How many liters of air are required to burn one liter of methane at the same temperature and pressure as the air? (*b*) If the pressure on the methane is two atmospheres and the air is one atmosphere, what volume of air is called for? (*c*) If the pressure on both is the same but the temperature of the air is 20° C. and the methane 0° C. what volume of air is called for? *Ans.* (*a*) 10 L.
(*b*) 20 L.
(*c*) 10.73 L.

178. 100 cc. of nitrous oxide (N_2O) at standard are decomposed into its elements and yields 150 cc. of a mixture of nitrogen and oxygen. 125 cc. of hydrogen at standard are now introduced and the mixture exploded, and the resultant volume found to be 125 cc. at standard. Show that the symbol must be N_2O.

179. 300 cc. of hydrogen and 100 cc. of nitrogen both at standard are combined to form ammonia gas in a closed system. If the volume of the resultant gas is 150 cc. and the pressure is unchanged, what is the temperature? *Ans.* −68.2° C.

180. 400 cc. of ammonia gas at standard are decomposed and the temperature reduced to standard. If the volume of the system is unchanged, what is the pressure on the resultant gas? *Ans.* 1520 mm.

181. 161.53 cc. of hydrogen at 18° C. and 754 mm. are united with 160.35 cc. of chlorine at 15° C. and 750 mm. What is the volume of the resultant gas at standard? *Ans.* 300 cc.

182. A liter of hydrogen at 39° C. is exploded with a liter of oxygen at 332.5 mm. The temperature is brought to 0° C. What volume of which gas is in excess? *Ans.* No excess.

183. 50 cc. of carbon monoxide are combined with oxygen in excess. After combination 60 cc. of gas remains. What was the volume of oxygen added? *Ans.* 35 cc.

184. 100 cc. of a mixture containing carbon monoxide and hydrogen are exploded with an excess of oxygen and 60 cc. of gas remain. Of this 60 cc., 40 cc. are absorbed by potassium hydroxide (the CO_2). What was the volume of the carbon monoxide, the hydrogen and the oxygen added?

Ans. 70 cc. O_2,
40 cc. CO,
60 cc. H_2.

185. If 50 cc. of ammonia gas at 15° C. and 766 mm. are decomposed into its elements, and 50 cc. of oxygen at 12° C. and 753 mm. are introduced, and the mixture exploded, what volumes of what gases remain at a temperature of 10° C. and 749 mm., disregarding the volume of water vapor formed?

Ans. 25.12 cc. N_2,
12.23 cc. O_2.

186. How many liters of oxygen at 10° C. and 765 mm. might be obtained by the decomposition of a liter of nitrogen pentoxide (N_2O_5) at 35° C. and 748 mm.? *Ans.* 2.246 L.

187. Given a mixture of hydrogen, carbon monoxide and nitrogen; calculate its percentage composition from the following:

Volume of mixture taken	25.00 cc.
Volume of oxygen added	10.00 cc.
Volume after explosion	22.50 cc.
Volume after CO_2 absorption	12.50 cc.

Ans. 20% H_2,
40% CO,
40% N_2.

188. Calculate the percentages of hydrogen, carbon monoxide and propane from the following:

Volume of sample taken	25.00 cc.
Volume after adding oxygen	100.00 cc.
Volume after explosion	55.50 cc.
Volume after CO_2 absorption	17.50 cc.

Ans. 28% H_2,
32% CO,
40% C_3H_8.

189. Calculate the composition of a gaseous mixture of carbon monoxide and acetylene from the following data:

Volume of mixture taken	20.00 cc.
Volume of oxygen added	50.00 cc.
Volume after explosion	52.00 cc.
Volume of oxygen left after KOH treatment	24.00 cc.

Ans. 8.00 cc. C_2H_2,
12.00 cc. CO.

190. Calculate the composition of a mixture of carbon monoxide and methane from the following:

Volume of mixture taken	20.00 cc.
Volume of oxygen added	40.00 cc.
Volume after explosion	47.00 cc.

Ans. 2.00 cc. CH_4,
18.00 cc. CO.

191. A gaseous mixture of oxygen, nitrous oxide (N_2O) and nitrogen is to be analyzed from the following:

Volume of mixture taken	20.00 cc.
Volume of hydrogen added	30.00 cc.
Volume after explosion	18.00 cc.
Volume of oxygen added	10.00 cc.
Volume after explosion	19.00 cc.

Ans. 8.00 cc. O_2,
8.00 cc. N_2O,
4.00 cc. N_2.

192. By means of the formulas developed on page 90, calculate the percentage composition of a mixture of hydrogen, carbon monoxide and methane, from the following:

Volume of mixture taken	50.00 cc.
Volume of oxygen added	75.00 cc.
Volume after explosion	60.00 cc.
Volume after absorption of CO_2	20.00 cc.

Ans. 20% H_2,
40% CO,
40% CH_4.

193. What is the weight of 300 cc. of nitric oxide (NO) under standard conditions? *Ans.* 0.40204 g.

194. What is the weight at standard of a liter of methane, the molecular weight of methane being 16.032?

Ans. 0.7159 g.

195. A liter of a gas at standard conditions weighed 3.627 g. What is its molecular weight? *Ans.* 81.22.

196. 963 cc. of a gas at 754.3 mm. and at 17° C. weigh 1.368 g. What is its molecular weight? *Ans.* 34.05.

197. Nitrogen has a molecular weight of 28.02. (*a*) What is the weight of a liter at standard conditions? (*b*) What is its specific gravity referred to $\frac{1}{32}$ oxygen? (*c*) To hydrogen?

Ans. (*a*) 1.251 g.
(*b*) 28.02.
(*c*) 13.90.

198. Bromine gas has a specific gravity, referred to air, of 5.524. What is its molecular weight? *Ans.* 159.9.

199. The density of hydrochloric acid referred to air is 1.2595. (*a*) What is its density referred to hydrogen? (*b*) To oxygen?

Ans. (*a*) 18.115.
(*b*) 1.1393.

200. The density of nitrogen at a certain pressure is 0.9802, referred to air at standard. (*a*) What is the pressure upon it? (*b*) What is its density at 15° C. and 760 mm. compared to air at standard? (*c*) If the density compared to air at standard is 0.9502, what is the temperature. (*d*) What is the density of nitrogen at 755 mm. and 150° C. compared to air at standard?

Ans. (*a*) 769.5 mm.
(*b*) 0.9177.
(*c*) 5.1° C.
(*d*) 0.6207.

201. A liter of ammonia gas under standard conditions weighed 0.7630 g. What is its specific gravity to hydrogen?

Ans. 8.4885.

202. A certain volume of chlorine weighs 0.6333 g.; if the same volume of silicon tetrafluoride weighs 0.9326 g., what is the molecular weight of the latter, taking the molecular weight of chlorine as 70.92? *Ans.* 104.44.

203. What is the volume at standard conditions of 1.008 g. of hydrogen? (*b*) Of 2.016 g.? *Ans.* (*a*) 11.2 L.
(*b*) 22.4 L.

204. The molecular weight of carbon monoxide is 28.00. What is its specific gravity to air? *Ans.* 0.9674.

205. What is the weight of 275 cc. of carbon oxysulphide (COS) at 15.5° C. and 768 mm.? *Ans.* 0.7054 g.

206. (*a*) What is the weight of 300 cc. of chlorine at standard conditions if its molecular weight is 70.92? (*b*) What is its specific gravity to $\frac{1}{32}$ oxygen? (*c*) To hydrogen? (*d*) To air? (*e*) To water? *Ans.* (*a*) 0.9501 g.
(*b*) 70.92.
(*c*) 35.24.
(*d*) 2.450.
(*e*) 0.003167.

207. A bulb known to hold exactly 500 cc., when filled with hydrogen at standard weighed (with all corrections) 30.04494 g.; when filled with ethane under the same conditions it weighed 30.67105 g. What is the molecular weight of ethane?
Ans. 30.05.

208. If the molecular weight of nitrous oxide is 44.02, at what pressure would 4 grams of this gas at 15° C. occupy a volume of one liter? *Ans.* 1631 mm.

209. Calculate the vapor density of carbon tetrachloride, compared with hydrogen, from the following readings obtained by the Hofmann method:

Weight of substance taken	0.2832 g.
Volume of vapor obtained	91.50 cc.
Temperature	99.50° C.
Barometer	746.9 mm.
Height of mercury in tube	283.4 mm.
Weight of a liter of hydrogen	0.089873 g.

Ans. 77.05.

210. Calculate the molecular weight of an organic substance from the following readings obtained by Hofmann's method:

Weight of substance taken	0.0835 g.
Volume of vapor obtained	81.40 cc.
Temperature	100° C.
Barometer	752.5 mm.
Height of mercury in tube	413.5 mm.

Ans. 70.38.

211. What is the vapor density, compared with air as unity, of iodine, yielding the following data when determined according to the method of Victor Meyer?

Weight of iodine taken	0.1735 g.
Volume of air displaced	17.40 cc.
Temperature	16° C.
Barometer	722.3 mm.
Tension of aqueous vapor at 16° C.	13.57 mm.

Ans. 8.757.

212. Victor Meyer's method yields the following results for carbon bisulphide. From them calculate the molecular weight.

Weight of carbon bisulphide taken	0.0825 g.
Volume of air displaced	27.34 cc.
Temperature	16.5° C.
Barometer	718 mm.
Tension of aqueous vapor at 16.5° C.	14.00 mm.

Ans. 77.38.

213. If air has a density of 0.0012926 referred to water: (*a*) What is its density at 754 mm.? (*b*) At 754 mm. and 38° C.? (*c*) At 770 mm. and −40° C.? *Ans.* (*a*) 0.0012824. (*b*) 0.0011257. (*c*) 0.0015344.

214. If the barometer at a certain place varied between 740 mm. and 785 mm. and the temperature varies between 40° C. and −40° C.: (*a*) What is the maximum variation in the density of the atmosphere if these variations work in conjunction? (*b*) What is the difference in the weight of a liter of air at

the greatest and the least density? (Density of the atmosphere = 0.0012926.) *Ans.* (*a*) 0.0004665.
(*b*) 0.4665 g.

215. A certain volume of silicon fluoride weighed 3.4962 g. The same volume of air under the same conditions weighed 0.9694 g. What is the molecular weight of the silicon fluoride? *Ans.* 104.4.

216. What is the specific gravity to air of hydrogen sulphide, the molecular weight of which is 34.086? *Ans.* 1.178.

217. The density of a gas is 0.8988 at 15° C. and 749 mm. What is its density at standard? *Ans.* 0.9621.

218. (*a*) At what temperature will one gram of hydrogen occupy a liter at 760 mm.? (*b*) At 750 mm.?
Ans. (*a*) − 248.42° C.
(*b*) − 248.79° C.

219. 283.5 cc. of a gas at 18° C. and 757 mm. weigh 0.51264 g. What is the weight of a liter at standard? *Ans.* 1.9351 g.

220. What is the weight at 20° C. and 767 mm. of 263 cc. of propylene (C_3H_6)? *Ans.* 0.4644 g.

221. If 283.5 cc. of hydrogen selenide (H_2Se) weigh 0.9497 g. at 17.4° C. and 747 mm., what is its molecular weight?
Ans. 81.19.

222. If 54.62 cc. of oxygen (density to hydrogen, 15.88) pass through a minute opening in the same time as 58.33 cc. of nitrogen: (*a*) What is the density of nitrogen to hydrogen? (*b*) Its molecular weight? *Ans.* (*a*) 13.93.
(*b*) 28.08.

223. 60.00 cc. of air effuse in the same time as 53.46 cc. of hydrochloric acid. What is the molecular weight of the hydrochloric acid? *Ans.* 36.45.

224. 76.42 cc. of sulphur dioxide pass through a minute orifice in the same time as 108.1 cc. of oxygen. What is the molecular weight of the sulphur dioxide? *Ans.* 64.03.

225. It required 75.2 seconds for a certain volume of hydrogen to pass through a minute orifice and 414.6 seconds for the

same quantity of carbon oxysulphide. (*a*) What is the density of the carbon oxysulphide to hydrogen? (*b*) Its molecular weight? *Ans.* (*a*) 30.4.
(*b*) 61.28.

226. It required 105.6 seconds for a certain volume of air to effuse and 39.3 seconds for the same quantity of helium. (*a*) What is the density of helium to air? (*b*) Its molecular weight? *Ans.* (*a*) 0.1385.
(*b*) 4.009.

227. It required 87.2 seconds for a certain volume of oxygen to pass through a minute orifice and 127.1 seconds for the same volume of boron fluoride. What is the molecular weight of the boron fluoride? *Ans.* 67.98.

228. How many grams of sulphuric acid must act on a metal to produce 1200 cc. of hydrogen at 0° C. and 760 mm., all of the hydrogen of the acid being liberated? *Ans.* 5.256 g.

229. If 15 g. of iron react with sulphuric acid thus:

$$Fe + H_2SO_4 = FeSO_4 + H_2,$$

how many liters of hydrogen are liberated at standard?
Ans. 6.017 L.

230. In the reaction:

$$CaCO_3 + 2\,HCl = CaCl_2 + CO_2 + H_2O.$$

(*a*) How many grams of calcium carbonate are required to produce 1700 cc. of carbon dioxide at 780 mm. and 17° C.? (*b*) If 860 cc. of carbon dioxide were liberated at 754 mm. and 20° C., how many grams of calcium carbonate were acted upon?
Ans. (*a*) 7.3376 g.
(*b*) 3.5515 g.

231. Lackawanna coal corresponds to the composition:

	Per cent
Volatile combustible matter	5.00
Carbon	84.00
Ash	11.00

Considering the volatile combustible matter to be methane, what volume of air at standard, $\frac{1}{5}$ of which is oxygen, is necessary to burn completely a kilogram? *Ans.* 8538.7 L.

232. Consider the coal of problem just preceding. If the heat of combustion of methane burned to carbon dioxide and water is 13,344 Calories and of carbon burned to carbon dioxide is 8080 Calories, what is the heat of combustion of this coal?

Ans. 7454.4 Cal.

233. From the equations:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$4\,HCl + MnO_2 = MnCl_2 + 2\,H_2O + Cl_2.$$

(*a*) What volume of chlorine measured under standard conditions will be produced by 10.000 g. of sodium chloride? (*b*) What volume of chlorine measured moist will be produced? (Ten. aq. vap. at 0° C. = 4.6 mm.) *Ans.* (*a*) 0.9579 L.
(*b*) 0.9637 L.

234. Consider the same reactions as in the previous problem. (*a*) One liter of chlorine measured at 764 mm. (the barometer not being corrected for temperature: brass scale) and 15° C., moist, indicates how much sodium chloride when the corrections are made? (*b*) How much sodium chloride is indicated if the readings are assumed to be correct as stated? (*c*) How many grams of sodium chloride are indicated if corrections were made for the pressure of water vapor and the temperature only? (Pressure of water vapor at 15° C. = 12.73 mm.: apparent expansion of Hg = 0.00017.) *Ans.* (*a*) 9.757 g.
(*b*) 9.948 g.
(*c*) 9.782 g.

235. If ten grams of water vapor occupy a volume of one liter, the pressure being 20 atmospheres, what is the temperature?

Ans. 166.1° C.

236. Water gas is produced according to the equation:

$$C + H_2O = CO + H_2.$$

(*a*) What volume of carbon monoxide and hydrogen will be produced from a kilogram of water? (*b*) What volume of carbon monoxide and hydrogen will be produced from a kilogram of carbon? (*c*) What volume of air is necessary for the

complete combustion of the gas produced in (*a*)? (Air = $\frac{1}{5}$ oxygen.)

Ans. (*a*) 2486.7 L.
(*b*) 3732.2 L.
(*c*) 6216.7 L.

237. A balloon has a capacity of 100,000 liters. How many kilograms of (*a*) sulphuric acid and (*b*) iron are necessary to fill the balloon with hydrogen at 20° C. and 760 mm.?

Ans. (*a*) 408 kg. H_2SO_4.
(*b*) 232.3 kg. Fe.

238. How many liters of air at standard are required for the combustion of one kilogram of a coal of the following composition?

	Per cent
Carbon	65.72
Hydrogen	9.03
Nitrogen	0.72
Oxygen	4.78
Ash	19.75

Ans. 8475 L.

239. Given a natural gas of the following composition by weight:

	Per cent
Hydrogen	1.42
Methane	94.16
Ethylene	0.30
Carbon dioxide	0.27
Carbon monoxide	0.55
Oxygen	0.30
Nitrogen	2.80
Hydrogen sulphide	0.18

How much air is necessary for the combustion of one kilogram?

Ans. 13,598 L.

240. A sample of calcium carbonate when treated with an acid evolved 200 cc. of carbon dioxide at 18° C. and 754 mm. How much calcium carbonate does this amount indicate?

Ans. 0.8316 g.

241. From the reaction,

$$2\,Mg + O_2 = 2\,MgO,$$

how many grams of magnesium can be burned in a globe containing 3489 cc. of oxygen at 19.5° C. and 768 mm.?

Ans. 7.145 g.

242. (*a*) What volume of nitrogen at 10° C. and 624 mm. is evolved from 3 liters of nitric oxide at 18° C. and 790 mm. when passed over red hot copper? (*b*) How many grams of copper oxide are formed? The reaction is

$$2\,NO + 2\,Cu = 2\,CuO + N_2.$$

Ans. (*a*) 1846.8 cc.
(*b*) 10.392 g.

243. (*a*) What volume of hydrogen at 17° C. and 748 mm. is required to unite with one gram of chlorine to form hydrochloric acid? (*b*) What volume of hydrogen under the same conditions but moist? (Ten. aq. vap. at 17° C. = 14.45 mm.)

Ans. (*a*) 0.3409 L.
(*b*) 0.3476 L.

244. How many cubic feet of hydrogen at 62° F. and 29.4″ will be yielded by the action of sulphuric acid on 10 lbs. of iron? *Ans.* 69.475 cu. ft.

245. 5 cubic feet of carbon dioxide measured at 70° F. and 30.7″ were evolved by the action of hydrochloric acid on calcium carbonate. How much calcium carbonate was decomposed? *Ans.* 1.326 lbs.

246. From the equation,

$$NH_4NO_3 = N_2O + 2\,H_2O,$$

(*a*) how many cubic feet of N_2O at standard will be produced by 15 lbs. of NH_4NO_3? (*b*) What is the resultant volume from the reaction at 30″ and 300° C.? *Ans.* (*a*) 67.16 cu. ft.
(*b*) 422.87 cu. ft.

247. A gas tank contains 200,000 cubic feet of dry coal gas at 30″ and 70° F. If 40% by volume of this is methane, how many pounds of methane are contained in the tank?

Ans. 3322 lbs.

248. How many cubic feet of oxygen and hydrogen together at standard result from the decomposition of $\frac{1}{4}$ lb. of water?

Ans. 7.46 cu. ft.

249. Six cubic feet of sulphur dioxide are required. (*a*) How many ounces of sulphuric acid and (*b*) copper are required? The reaction is

$$Cu + 2\,H_2SO_4 = CuSO_4 + 2\,H_2O + SO_2.$$

Ans. (*a*) 52.54 oz.
(*b*) 17.03 oz.

250. How many cubic feet of air at standard are required to burn a ton of 2000 lbs. of coal gas of the following composition by weight?

	Per cent
Hydrogen	45.85
Methane	39.26
Ethylene	5.17
Carbon dioxide	0.82
Carbon monoxide	4.78
Oxygen	0.41
Nitrogen	3.71

Ans. 605,515 cu. ft.

251. If the reaction for the decomposition of oxalic acid proceeded as follows:

$$2\,(C_2H_2O_4 \cdot 2\,H_2O) = HCOOH + 5\,H_2O + 2\,CO_2 + CO,$$

and the products were brought to standard conditions, (*a*) what is the volume of the gases (neglecting the volume of water vapor present) if 2 oz. of oxalic acid are decomposed?[1] (*b*) If the temperature is now raised to 140° C., what is the volume of the gases formed, pressure remaining at standard? (*c*) If the formic acid decomposes at 160° C. as follows:

$$HCOOH = CO_2 + H_2,$$

what is the total volume of the gases formed at 200° C.?

Ans. (*a*) 0.5332 cu. ft.
(*b*) 2.420 cu. ft.
(*c*) 3.072 cu. ft.

[1] Water freezes at 0° C. and boils at 100° C.; formic acid melts at 8.6° C. and boils at 100.8° C.

252. A flask weighs 139.8460 g. in air with brass weights (density, 8.4). The temperature is 18° C., the barometer 757 mm. The density of the flask is 3.45. What is the weight *in vacuo*? (Use the decimal coefficient of expansion of a gas. 1 cc. air at standard weighs 0.0012926 g.) *Ans.* 139.8748 g.

253. A flask and water are counterpoised by 1008.2600 g., the weights being of brass (density, 8.4). The temperature is 18° C., the barometer 634 mm. Regarding the flask and water as having a density of 1, what is the weight *in vacuo*?

Ans. 1009.1586 g.

254. It is desired to weigh out an amount of platinum (sp. gr., 21.5) in air at 17° C. and 764 mm. so that its true weight *in vacuo* should be 200.0000 g. Brass weights are used (density, 8.4). What weight should be put on the other pan? (Use the decimal coefficient of expansion.) *Ans.* 200.01774 g.

255. It is desired to weigh out 576.4213 g. to be true *in vacuo*. Brass weights (density, 8.4) are used, the temperature is 19° C., the barometer 764 mm. The density of the body to be weighed is 2.637; what weight must be put on the other side? (Use the decimal coefficient of expansion of a gas.) *Ans.* 576.2391 g.

256. It is required to get a weight of water that will be true *in vacuo*. Brass weights are used (density, 8.4), the density of the water is 0.999050, the weight required is 100.2037 g., the temperature of the air is 18° C. and the barometer is 763 mm. What weight must be put on the other pan? (Use the decimal coefficient of expansion of a gas.) *Ans.* 100.0961 g.

257. A flask of glass (density, 3.4) [1] weighing 203.8050 g. in air is filled with water at 17° C. when it weighs 1397.4370 g. in air, the temperature being 17° C., the barometer 756 mm.; brass weights are used (density, 8.4). What is the weight *in vacuo* of the combination? (Use the decimal coefficient of expansion of a gas. Density of water at 17° C. = 0.9988.)

Ans. 1398.75 g.

[1] Take into account the weight of air displaced by the glass of the flask.

258. (*a*) Calculate $Wd\left(\frac{1}{D'} - \frac{1}{D}\right)$[1] for a cubic centimeter of water weighed in air under the following conditions:

Temperature of the air	15° C.
Temperature of the water	15° C.
Barometric pressure	770 mm.
Saturation of aqueous vapor in the air	50%
Vapor pressure of water vapor at 15° C.	12.728 mm.
Coefficient of expansion of air	0.00367
Weight of a liter of dry air at 0° C. and 760 mm.	1.2926 g.
Density of water at 15° C.	0.999126
Density of weights	8.4
Coefficient of cubical expansion of glass	0.000025

(*b*) Using this last calculated quantity, calculate the apparent weight, in air, of 250 cc. of water under these conditions. (*c*) If a flask marked 250 cc. at 20° C. (United States Standard) gives an apparent weight of water in air under the conditions enumerated above of 249.508 g., what is the error of the flask?

Ans. (*a*) 0.0010903.
(*b*) 249.508 g.
(*c*) 0.031 cc.

259. Calculate the weight of a liter of water in air under the following conditions:

Temperature of the air	20° C.
Temperature of the water	20° C.
Barometric pressure	760 mm.
Saturation of aqueous vapor in the air	50%
Weight of a liter of dry air at 0° C. and 760 mm.	1.2926 g.
Vapor pressure of water at 20° C.	17.406 mm.
Density of water at 20° C.	0.998230
Density of weights	8.4
Coefficient of expansion of air	0.00367

Ans. 997.173 g.

260. A flask calibrated to contain 500 cc. at 20° C. (United States Standard) was found to hold 499.149 g. of water when filled to the mark. The flask was tared with a similar flask,

[1] See p. 104.

finishing the tare with glass beads, foil, etc. Given the following conditions, what is the error of the flask?

Temperature of water and flask	17° C.
Temperature of air	17° C.
Barometric pressure	760 mm.
Saturation of aqueous vapor	50%
Tension of aqueous vapor at 17° C.	14.45 mm.
Weight of a liter of dry air at 0° C. and 760 mm.	1.2926 g.
Coefficient of expansion of air	0.00367
Density of water at 17° C.	0.998801
Density of weights	8.4
Cubical coefficient of expansion of glass	0.000025

Ans. +0.15 cc.

261. A flask is to be calibrated to hold 2000 cc. at 20° C. (United States Standard). It is tared by a similar flask, finishing the tare with glass beads, foil, etc. How many grams of water should be weighed into the flask under the following conditions?

Temperature of water and flask	17° C.
Temperature of air	17° C.
Barometric pressure	752 mm.
Saturation of aqueous vapor in the air	38%
Vapor tension of water at 17° C.	14.45 mm.
Coefficient of expansion of air	0.00367
Weight of a liter of air at 0° C. and 760 mm.	1.2926 g.
Density of water at 17° C.	0.998801
Density of weights	8.4
Cubical coefficient of expansion of glass	0.000025

Ans. 1995.64 g.

262. (*a*) What is the volume of one gram of water at 15° C., weighed in air with brass weights (density, 8.4), the temperature of the air being 15° C., pressure of the atmosphere 760 mm. (*b*) What is the volume of a kilogram of water under these conditions? (Use the decimal coefficient of expansion of a gas. Density of water at 15° C. = 0.999126: weight of one cubic centimeter of air at standard = 0.0012926 g.)

Ans. (*a*) 1.001954 cc.
(*b*) 1001.954 cc.

263. A flask calibrated to hold one Mohr's liter at 15° C. was counterpoised by another similar flask and sand. Filling up to the mark with water at 15° C. and 760 mm. required 999.8730 g. What is the error? *Ans.* −0.127 cc.

264. (*a*) What is the volume of one gram of water at 60° F., weighed in air with brass weights (density, 8.4), the temperature of the air being 60° F., the barometer standing at 760 mm. (*b*) What is the weight of a kilogram of water under these conditions? (Use the decimal coefficient of expansion of a gas. Density of water at 60° F. = 0.999050.)

Ans. (*a*) 1.002037 cc.
(*b*) 1002.037 cc.

265. If air is saturated with water vapor at 20° C. and 760 mm.: (*a*) What per cent of its volume is aqueous vapor? (*b*) Taking air to have a molecular weight of 28.943, what is the weight of a liter of saturated air at this temperature? (*c*) What is its density referred to water? (Ten. aq. vap. at 20° C. = 17.41 mm.) *Ans.* (*a*) 2.291%.
(*b*) 1.194 g.
(*c*) 0.001194.

266. The temperature of a room is 18° C., the dew point is 15° C. What is the humidity? (Ten. aq. vap. at 18° C. = 15.38 mm.; at 15° C. = 12.73 mm.) *Ans.* 83%.

267. (*a*) What is the mass of nitrogen in a liter of nitrogen measured moist at 18° C. and 763 mm.? (*b*) What is the mass of the water vapor disseminated throughout the liter? (*c*) What is the mass of the moist nitrogen? (Ten. aq. vap. at 18° C. = 15.38 mm.) *Ans.* (*a*) 1.1548 g.
(*b*) 0.1527 g.
(*c*) 1.3075 g.

268. (*a*) What is the weight of a liter of water vapor saturated at 15° C. and 760 mm.? (*b*) What is its density compared to water at 4° C. (Ten. aq. vap. at 15° C. = 12.73 mm.)

Ans. (*a*) 0.01277 g.
(*b*) 0.00001277 g.

269. (*a*) What is the mass of a liter of saturated air at 15° C. and 730 mm.? (*b*) What is the percentage by weight of air and moisture in air under these conditions? (Use the decimal coefficient of expansion of a gas. Ten. aq. vap. at 15° C. = 12.73 mm.) *Ans.* (*a*) 1.1690 g.
(*b*) 98.91% air.
1.09% H_2O.

270. The humidity at 25° C. is 83%; the barometer stands at 765 mm. If the temperature were to suddenly drop to 15° C. and the barometer to 755 mm., how much moisture would be precipitated per cubic meter? (Ten. aq. vap. at 15° C. = 12.73 mm.; at 25° C. = 23.55 mm.) *Ans.* 1.669 g.

271. How many grams of water will evaporate into a five liter space at 20° C. and 760 mm.? (First calculate the density of the aqueous vapor at 20° C. to water at 4° C.; ten. aq. vap. at 20° C. = 17.41 mm.) *Ans.* 0.0860 g.

272. (*a*) What weight of water vapor is present in a cubic meter of air saturated at 20° C.? (*b*) If the relative humidity is 60%? (*c*) If the air has a relative humidity of 80% at 20° C. and should be cooled to 10° C., what weight of water would be precipitated per cubic meter? (Density of aqueous vapor at 20° C. = 0.0000172; at 10° C. = 0.0000093.)
Ans. (*a*) 17.2 g.
(*b*) 10.32 g.
(*c*) 4.46 g.

273. What is the weight of a liter of air at 18° C. and 762 mm., the dew point being 15° C.? (Ten. aq. vap. at 15° C. = 12.73 mm.) *Ans.* 1.2050 g.

274. Calculate the weight of a liter of air 45% saturated with water vapor at 765 mm. and 18° C. (Tension of aqueous vapor at 18° C. = 15.38 mm. Weight of a liter of dry air at 760 mm. and 0° C. = 1.2926 g.) *Ans.* 1.2165 g.

275. Calculate the weight of a liter of carbon dioxide at 20° C. and 772 mm., the gas being 50% saturated with water

vapor. (Tension of aqueous vapor at 20° C. = 17.41 mm. Weight of a liter of dry carbon dioxide at 0° C. and 760 mm. = 1.9768 g.) *Ans.* 1.8585 g.

276. Using the symbols of page 109, deduce the approximate formula $W_{g+w} = \frac{P'_{g+w} - 0.6\,P'_w}{760} \times \frac{273}{T'} \times 1.9768$ for the calculation of the volume of moist carbon dioxide at any temperature and pressure to the volume dry at 0° C. and 760 mm. (Weight of a liter of dry carbon dioxide at 0° C. and 760 mm. = 1.9768 g.)

CHAPTER VII

CALCULATION OF ATOMIC WEIGHTS AND FORMULAS

Atomic Weight. — The atomic weight of an element is the ratio of the weight of an atom of that element to the weight of an atom of some other element taken as standard. This standard is oxygen which is arbitrarily given an atomic weight of 16. Hydrogen, the lightest of the elements, was formerly taken as unity, but this unit has been abandoned and oxygen has supplanted it, for the reason that most of the elements form binary and other compounds with oxygen which are stable at ordinary temperatures, while the same is not true of hydrogen. Again, it happens that when oxygen is taken as 16, more of the atomic weights of the elements can be expressed in whole numbers than is the case when the hydrogen standard is employed, and also there are more compounds of importance to the chemist, containing oxygen, than hydrogen.

Valence. — Valence is the power of an atom of an element to combine with a certain number of atoms of another element, taking the valence of hydrogen as unity. Valence is a numerical property of an element by virtue of which a definite number of atoms of another element are held in combination.

Combining Weight. — The combining weight of an element is the weight of that element which will combine with, replace or be replaced by, 16 parts by weight of oxygen.

Radicals or ions may be considered to have valence. Thus, sulphuric acid has two replaceable hydrogens, so the radical SO_4 is divalent: the hydroxyl radical, OH, combines with one atom of hydrogen to form water, one atom of sodium to form sodium hydroxide and, consequently, has a valence of one.

Relationship between Atomic Weight, Valence and Combining Weight. — As oxygen has a valence of two, the following equation shows the relationship between the atomic weight, the combining weight and the valence of elements

$$A = \frac{C}{2} V,$$

in which A is the atomic weight, C the combining weight[1] and V the valence.

Calculation of Atomic Weight from an Analysis. Simple Cases. — For example, mercury and oxygen have each a valence of two, the compound mercuric oxide is HgO, which by analysis gives: 92.61% mercury and 7.39% oxygen. Then X grams of mercuric oxide contain $0.926\,X$ g. of mercury and $0.074\,X$ g. of oxygen. The equivalent of mercury according to definition is

$$\frac{0.9261\,X}{0.0739\,X} \times 16 = \frac{0.9261}{0.0739} \times 16 = 200.6.$$

[1] Combining weights may be referred to other elements than oxygen. If x represents the valence of the element to which the combining weight is referred, then the formula becomes $A = \frac{C}{x} V$. The term "equivalent" is often employed and by it is meant that weight of an element which will combine with, replace or be replaced by 8 parts by weight of oxygen. With this definition the formula becomes $A = CV$. This latter is frequently used, but the formula given in the text is employed for the reason that it refers to oxygen as 16, which is the arbitrary standard to which all atomic and molecular weights are referred.

Substituting in the equation, the atomic weight is

$$A = \frac{200.6}{2} \times 2 = 200.6.$$

Again, iron in its trivalent form is combined with oxygen yielding an oxide which on analysis shows 30.06% oxygen, 69.94% iron Then, as before, the equivalent of the iron is

$$\frac{0.6994}{0.3006} \times 16 = 37.23,$$

and the atomic weight of iron is

$$A = \frac{37.23}{2} \times 3 = 55.84.$$

Law of Dulong and Petit. — The formula $A = \frac{C}{2} V$[1] supposes a knowledge of the valence of the element the atomic weight of which is to be calculated. The combining weight is found by an analysis of a compound, preferably a compound of the element with oxygen, if such compound be stable. In the case of compounds of elements which cannot be vaporized without decomposition, a knowledge of the valence of the element must be determined by other means than through molecular weights determined by vapor density methods. For this the law of Dulong and Petit is employed. This law states that the product of the atomic weight of an element into its specific heat (in the solid state) is a constant. The product is called the atomic heat and its value approximates 6.4.[2] If w represents the atomic weight and S the specific heat, the law may be symbolized:

$$\text{Atomic heat} = Sw = 6.4.$$

[1] P. 142.

[2] Exceptions occur, notably in the cases of carbon, silicon, beryllium and boron.

consequently, the atomic weight of sodium is

$$\frac{3.9343}{6.0657} \times 35.46 = 23.00.$$

The molecular weight of a substance is the sum of the atomic weights of the atoms entering into the molecule. When a substance may be vaporized without decomposition, the molecular weight is obtained as given in the section devoted to gas densities.

Molecular Weight by Elevation of Boiling Point and Depression of Freezing Point. — In addition to the method of measuring vapor densities, there are two methods commonly employed with non-electrolytes (*i.e.*, substances which do not ionize appreciably upon going into solution). These may be determined, in general, by measuring the depression of the freezing point and the elevation of the boiling point, due to the introduction of a solute.

The depression of the freezing point of a given amount of solvent is the same for a gram-molecule of substance, and, in general, is independent of the composition of the substance if no ionization takes place. The amount of this depression depends upon the nature of the solvent. Let M be the molecular weight of the dissolved substance, ω its weight in grams, W the weight of the solvent in grams, Δ the observed change of temperature and K a constant depending upon the nature of the solvent. The molecular weight is given by the formula

$$M = K\frac{\omega}{\Delta W}.$$

Using the symbols with the same meaning, as above, for the determination of molecular weights from the raising of the boiling point, the same formula applies except that K is a different constant and Δ represents

the elevation of the boiling point of the solvent due to the introduction of the solute. Below are a few values for K:

Solvent.	K Dep. of F. P.	K Elev. of B. P.
Water	1850	510
Benzol	5000	2610
Ethyl ether	.....	2160
Chloroform	.....	3590

Molecular Weight of an Organic Acid from Analysis of the Silver Salt. — A method for the determination of molecular weights particularly applicable to organic acids is illustrated as follows:[1] One gram of silver acetate on analysis is found to contain 0.6464 g. of silver. As silver is univalent, then one hydrogen must have been replaced for each acidic hydrogen ion in the acetic acid, which being a monobasic acid has one replaceable hydrogen ion. It is evident that in this compound there are

$$1.0000 - 0.6464 = 0.3536 \text{ g.}$$

of substance other than silver; the molecular weight of the radical is

$$\frac{0.3536}{0.6464} \times 107.88 = 59.015.$$

The weight of the acetic acid, then, must be

$$59.015 + 1.008 = 60.02.$$

Molecular Weight of an Organic Base from Analysis of the Hydrochloro Platinic Acid Salt. — The molecular weight of an organic base may be determined by weigh-

[1] Strictly speaking, this method presupposes a knowledge of the number of replaceable hydrogen atoms and in reality only gives the molecular weight of the empirical formula of the acid.

ing the hydrochloro platinic acid salt of the base, igniting, and weighing the residue of platinum after ignition.[1] The formation of the salt may be symbolized (letting B represent the organic base) as follows:

$$2\,B + H_2PtCl_6 = B_2H_2PtCl_6.$$

One gram of methyl amine hydrochloro platinic acid leaves 0.4134 g. of platinum after ignition. To calculate the molecular weight of methyl amine, let x represent the molecular weight of methyl amine, then

$$\frac{1.0000}{0.4134} = \frac{2x + H_2PtCl_6}{Pt} = \frac{2x + 409.98}{195.2}.$$

Solving gives $x = 31.08$.

Formula of Compound, Given Molecular Weight and Percentage Composition. — The molecular formula of a compound is easily determined, knowing the molecular weight and the percentage composition. Take, for example, barium dichromate, given the following:

Molecular weight	353.57
Barium	38.85%
Chromium	29.47%
Oxygen	31.68%

The proportion of barium in the molecule is (atomic weight = 137.37)

$$\frac{38.85}{100.00} \times 353.57 = 137.37, \quad \frac{137.37}{137.37} = 1;$$

of chromium (atomic weight = 52.1),

$$\frac{29.47}{100.00} \times 353.57 = 104.2, \quad \frac{104.2}{52.1} = 2;$$

of oxygen (atomic weight = 16.00),

$$\frac{31.68}{100.00} \times 353.57 = 112, \quad \frac{112}{16} = 7.$$

Consequently, the symbol is $BaCr_2O_7$.

[1] This method presupposes the organic base to be mono acidic.

Formula from Percentage Composition. — Formulas may be empirical or molecular. The *empirical* formula is the simplest formula that can be assigned the substance and, in general, is only used in the absence of knowledge of the molecular formula. The *molecular* formula shows the number of atoms in the molecule and consequently indicates the molecular weight, that is, that weight of substance which in the gaseous state would occupy 22.4 liters. To calculate the empirical formula of a compound, let

A = symbol of one of the elements present in a compound;

B = symbol of another element present in the same compound;

C = symbol of still another element present in the same compound.

x = subscript of A in the compound under consideration;

y = subscript of B in the compound under consideration;

z = subscript of C in the compound under consideration.

a = atomic weight of the element A;

b = atomic weight of the element B;

c = atomic weight of the element C.

$A_xB_yC_z$ = molecular symbol of the compound under consideration.

Then the molecular weight of the compound is $ax + by + cz$. Let this be represented by M. Then

$$\%A = \frac{ax}{M} \times 100; \quad \%B = \frac{by}{M} \times 100; \quad \%C = \frac{cz}{M} \times 100.$$

Then

$$\%A : \%B : \%C = \frac{ax}{M} \times 100 : \frac{by}{M} \times 100 : \frac{cz}{M} \times 100,$$

$$= ax : by : cz.$$

Hence

$$\frac{\%A}{a} : \frac{\%B}{b} : \frac{\%C}{c} = x : y : z.$$

Then

$$x = K\frac{\%\,A}{a}, \qquad y = K\frac{\%\,B}{b}, \qquad z = K\frac{\%\,C}{c},$$

in which K is a constant. Multiples of K are chosen which will give x, y and z integral values.

To apply the above, suppose a substance analyzes

	Per cent
Carbon	40.0
Hydrogen	6.6
Oxygen	53.4

Then if x, y and z represent the subscripts of carbon, hydrogen and oxygen respectively,

$$x = \frac{40.0}{12} = 3.3$$

$$y = \frac{6.6}{1} = 6.6$$

$$z = \frac{53.4}{16} = 3.3$$

As there cannot be less than one atom of each element present, it is evident that the ratio of the atomic weights of carbon, hydrogen and oxygen in this compound must be one atomic weight of carbon, one atomic weight of oxygen and two atomic weights of hydrogen, and the *empirical* or simplest formula is CH_2O, corresponding to a molecular weight of 30.[1] Such a compound is known and is formaldehyde (oxymethylene). The compound might, however, be $(CH_2O)_x$, and in the absence of knowledge of the value of x no further information may be

[1] The value of K in this example is $\frac{1}{3.3}$. Multiplying the values obtained for x, y and z by this quantity gives integral values for x, y and z of 1, 2 and 1 respectively. A value for K need not be determined as will be seen later.

It is not necessary to have the composition of the compound expressed in percentages. For instance, the same result is obtained

conveyed than is given in the empirical formula. There is a compound yielding the same percentage composition which shows a molecular weight of 60 and corresponds to the molecular symbol $C_2H_4O_2$ (acetic acid). In this case the value of x is two. Another compound, which on analysis has the same composition and has a molecular weight of 90, corresponds to the formula $C_3H_6O_3$ and is lactic acid. Finally, there is still another compound of molecular weight 180, being grape sugar, $C_6H_{12}O_6$, in which the value of x is six. When the molecular weight of a compound is known the molecular formula may be calculated: when this is lacking, given the percentage composition of a compound, in the absence of other knowledge, the empiric formula only may be determined. A complex case will now be considered. A compound analyzes:

	Per cent
Carbon	49.97
Hydrogen	6.46
Nitrogen	17.95
Oxygen	25.62
	100.00

---

from the following analysis of this same compound, 2.6000 g. of substance being taken:

Carbon	1.0400 g.
Hydrogen	0.1716 g.
Carbon	1.3884 g.
	2.6000 g.

Then

$$C = \frac{1.0400}{12} = 0.08667 = 1,$$

$$H = \frac{0.1716}{1.008} = 0.17024 = 2,$$

$$O = \frac{1.3884}{16} = 0.08679 = 1,$$

as before.

To calculate its empiric formula. As before,

$$C = \frac{49.02}{12} = 4.164,$$

$$H = \frac{5.46}{1.008} = 5.406,$$

$$N = \frac{17.95}{14.01} = 1.281,$$

$$O = \frac{25.52}{16} = 1.601.$$

The compound, then, corresponds to the formula $C_{4.164}H_{5.406}N_{1.281}O_{1.601}$. But a formula must express the ratio of the atoms in simple whole numbers, the problem now presented being to find this ratio. It is apparent that the nitrogen atoms are present in the smallest number; then taking nitrogen as unity as in *a* :

	a	*b*
C	$\frac{4.164}{1.281} = 3.250$[1]	$\frac{4.164}{0.6405} = 6.501$
H	$\frac{6.406}{1.281} = 5.000$	$\frac{6.406}{0.6405} = 10.00$
N	$\frac{1.281}{1.281} = 1.000$	$\frac{1.281}{0.6405} = 2.000$
O	$\frac{1.601}{1.281} = 1.250$	$\frac{1.601}{0.6504} = 2.500$

[1] The ratios in (*a*) assume nitrogen to be present to the extent of one atomic weight. With this assumption it is seen that the other elements are not present as whole but as fractional atomic weights, which, according to the atomic theory, cannot be. The ratios of (*b*), (*c*) and (*d*) may be arrived at by multiplying these ratios by 2, 3 and 4 respectively. Finally, a series of ratios approximating whole numbers is reached.

	(*c*)	(*d*)
C	$\frac{4.164}{0.4270} = 9.752$	$\frac{4.164}{0.32025} = 13.002 = 13$
H	$\frac{6.406}{0.4270} = 15.00$	$\frac{6.406}{0.32025} = 20.004 = 20$
N	$\frac{1.281}{0.4270} = 3.000$	$\frac{1.281}{0.32025} = 4.000 = 4$
O	$\frac{1.601}{0.4270} = 3.750$	$\frac{1.601}{0.32025} = 5.000 = 5$

From (*a*) the formula would be $C_{3.25}H_5N_1O_{1.25}$. This ratio is not, in whole numbers. Determining the ratio on the assumption that two nitrogens are present (by dividing the nitrogen ratio, 1.281, by 2, giving the quotient 0.6405 and dividing through by this), the formula $C_{6.5}H_{10}N_2O_{2.5}$ is obtained (*b*). Taking nitrogen as being present to the extent of three atoms, the ratio as found in (*c*) is $C_{9.75}H_{15}N_3O_{3.75}$. Assuming four nitrogen atoms to be present, the ratio numbers of (*d*) yield $C_{13}H_{20}N_4O_5$. The case cited has been carried to the end and this method must yield results finally, but only on the assumption that the percentage composition as given is correct. That this ratio would finally have been reached might have been seen by an inspection of the ratios of (*a*). These ratios (*a*), it will be observed, are all evenly divisible by 0.25; consequently, dividing the ratios through by this number would have led to the result, $C_{13}H_{20}N_4O_5$, by inspection, obviating the necessity of calculating (*b*), (*c*) and (*d*).[1] Such a short cut is not always apparent at a

[1] The process amounts to finding the approximate lowest common multiple of the subscripts. Knowing the lowest common multiple, by dividing the subscripts by it, the numbers so obtained

The calculation of its formula is

$$K_2O = \frac{9.93}{94.2} = 0.1054 : \frac{0.1054}{0.1054} = 1,$$

$$Al_2O_3 = \frac{10.77}{102.2} = 0.1054 : \frac{0.1054}{0.1054} = 1,$$

$$SO_3 = \frac{33.72}{80.07} = 0.4211 : \frac{0.4211}{0.1054} = 4,$$

$$H_2O = \frac{45.56}{18.016} = 2.529 : \frac{2.529}{0.1054} = 24,$$

and the compound is $K_2O \cdot Al_2O_3 \cdot 4\,SO_3 \cdot 24\,H_2O$, or it may be written: $K_2O \cdot SO_3 : Al_2O_3 \cdot 3\,SO_3 : 24\,H_2O$ $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24\,H_2O$, or $KAl(SO_4)_2 \cdot 12\,H_2O$.

In the problem above, the analysis is supposed to be correct as given. In practice, the analysis of a substance will contain errors, large or small, according to the accuracy of the methods employed and the difficulties encountered in the determination of the various constituents. Where the constituents are present in about equal amounts and all the constituents are determined with the same degree of accuracy, it is easier to find the ratios of the atoms or radicals by the method already given. In many cases, one or more constituents are present to but a small extent, or the methods by which they were determined do not lend themselves to the same degree of nicety of determination as with some of the other constituents present. In the calculation of formulas many things must be taken into account and it is largely a matter of judgment as to the manner of calculation. These facts, the method of preparation or the manner of formation of the compound, its similarity to other well-known compounds of the same type, the methods employed in the analysis: all these must be taken into account, leaving the determination

of the formula of a compound to a large degree a matter of judgment. Suppose a substance on analysis yields

	Per cent
Manganese	24.50
Hydrogen	1.02
Arsenic	45.07
Oxygen (by diff.)	29.41

and let it be assumed that the arsenic is determined with the greatest degree of accuracy. Then

$$\text{Mn} = \frac{24.50}{54.93} = 0.446,$$

$$\text{H} = \frac{1.02}{1.008} = 0.902,$$

$$\text{As} = \frac{45.07}{74.96} = 0.602,$$

$$\text{O} = \frac{29.41}{16} = 1.838,$$

and the compound approximates $Mn_{0.446}As_{0.601}O_{1.838}H_{0.902}$. It is required to find the ratio of simple whole numbers which approximates these ratios. By inspection it will be noted that the ratio of manganese to hydrogen is approximately 1 : 2. Also it can be seen that the ratio of hydrogen to arsenic is nearly 3 : 2. Then it is evident that if these numbers representing the ratios found by analysis are divided by 0.15 that the ratios of manganese, hydrogen and arsenic fall into approximately even numbers. This would indicate the arsenic to be present to the extent of four atoms $\left(\frac{0.60}{0.15} = 4\right)$. Then, proceeding on this assumption:

$$\text{Mn} = \frac{0.446}{0.15} = 2.97 = 3 \text{ very closely,}$$

$$\text{H} = \frac{0.902}{0.15} = 6.01 = 6 \text{ very closely,}$$

$$\text{As} = \frac{0.602}{0.15} = 4.01 = 4 \text{ very closely,}$$

$$\text{O} = \frac{1.838}{0.15} = 12.2 = 12 \text{ very closely.}$$

Consequently, the compound is $Mn_3H_6As_4O_{12}$ or $Mn_3H_6(AsO_3)_4$.

Formulas of Minerals. Isomorphic Replacement. — A definite crystalline structure generally indicates purity and, consequently, definite chemical composition. Mitscherlich propounded the law that: "Substances which are analogous chemical compounds have the same crystalline form"; in other words, they are isomorphous. To a large extent this is true, but there are so many exceptions that the statement cannot be called a law. The "alums" consist of sulphates of a trivalent and a monovalent base with twelve molecules of water, all crystallizing isomorphously. By manipulation a crystal may be grown to contain one or more alums. Such crystals will not show definite chemical composition, but are mixtures, and may be regarded as a single alum, parts of which have been replaced by an analogous substance. This is isomorphous replacement.

Strict rules for isomorphous replacement cannot be given. In general, it may be said that metals and metallic oxides of the same structure can replace each other and the same is true of the non-metals and acidic oxides. Thus Al_2O_3 and Fe_2O_3 are mutually replaceable as are the oxides FeO, MgO, CaO, MnO, etc., these latter being similar in being oxides of divalent metals. In like manner

the alkalies, NH_4, Li, Na, K, etc., and their oxides $(NH_4)_2O$, Li_2O, Na_2O, K_2O, etc., may replace each other in a mineral. This is not all — CaO, for example, may be replaced by K_2O or another alkali oxide, as also, in some instances, FeO may be replaced by Al_2O_3. This leaves the matter to a large extent one of judgment: for more complete information the student is referred to works on mineralogy. The more common cases follow the rule of compounds of like structure replacing each other.

Mosander examined a specimen of Menaccanite and found it to be composed of

	Per cent
TiO_2	46.92
Fe_2O_3	10.74
FeO	37.86
MnO	2.73
MgO	1.14
	99.39

The percentages of the metals and oxygen are

$$\frac{\text{Ti}^1}{\text{TiO}_2} = \frac{48.1}{80.1} \times 46.92 = 28.18\%\ \text{Ti} \quad \text{and } 18.74\%\ \text{O},$$

$$\frac{2\,\text{Fe}}{\text{Fe}_2\text{O}_3} = \frac{2\,(55.85)}{159.70} \times 10.74 = 7.51\%\ \text{Fe} \quad \text{and } 3.23\%\ \text{O},$$

$$\frac{\text{Fe}}{\text{FeO}} = \frac{55.85}{71.85} \times 37.86 = 29.44\%\ \text{Fe} \quad \text{and } 8.42\%\ \text{O},$$

$$\frac{\text{Mn}}{\text{MnO}} = \frac{54.93}{70.93} \times 2.73 = 2.12\%\ \text{Mn} \quad \text{and } 0.61\%\ \text{O},$$

$$\frac{\text{Mg}}{\text{MgO}} = \frac{24.32}{40.32} \times 1.14 = 0.68\%\ \text{Mg} \quad \text{and } 0.45\%\ \text{O},$$

$$\text{Total} \qquad 31.45\%\ \text{O}.$$

[1] These calculations are very easily performed by the use of the slide rule, as the error of the rule is, on the average, less than the error of analysis, etc. For the same reason approximate atomic weights may be used.

If the metals replaced iron, the percentages replaced are

$$\frac{Fe}{Ti} = \frac{55.85}{48.1} \times 28.18 = 32.71\% \text{ Ti as Fe},$$

$$\frac{Fe}{Mn} = \frac{55.85}{54.93} \times 2.12 = 2.16\% \text{ Mn as Fe},$$

$$\frac{Fe}{Mg} = \frac{55.85}{24.32} \times 0.68 = 1.58\% \text{ Mg as Fe},$$

$$36.45 + 36.95 = 73.40\% \text{ total Fe}.$$

$$Fe = \frac{73.40}{55.85} = 1.314 : \frac{1.314}{0.657} = 2.00,$$

$$O = \frac{31.45}{16.00} = 1.976 : \frac{1.976}{0.657} = 2.99 = 3 \text{ approx.}$$

This mineral, considered as an oxide of iron,[1] approximates very closely to the formula Fe_2O_3 (hematite), part of the iron being replaced by other metals, chiefly titanium, making it $(TiFe)_2O_3$. The mineral as it analyzes is $(Ti, Fe, Mn, Mg)_2O_3$. An inspection of the analysis would show that there are no distinctively acid oxides present, which would suggest the method of calculation adopted.

[1] The metals could just as well be calculated on the supposition that they replaced titanium:

$$\frac{Ti}{Fe} = \frac{48.1}{55.85} \times 36.95 = 31.82\% \text{ Fe as Ti},$$

$$\frac{Ti}{Mn} = \frac{48.1}{54.93} \times 2.12 = 1.86\% \text{ Mn as Ti},$$

$$\frac{Ti}{Mg} = \frac{48.1}{24.32} \times 0.69 = 1.37\% \text{ Mg as Ti},$$

$$35.05 + 28.18 = 63.23\% \text{ total Ti}.$$

$$Ti = \frac{63.23}{48.1} = 1.315 = 2 \text{ approximately},$$

$$O = \frac{31.45}{16} = 1.966 = 3 \text{ approximately},$$

and the mineral becomes Ti_2O_3, or more generally M_2O_3, as before.

Given the following analysis by Pisani, to determine the formula of the mineral.

	Per cent
SiO_2	45.95
Al_2O_3	0.85
FeO	8.91
MnO	10.20
ZnO	10.15
CaO	21.55
MgO	3.61
Loss on ignition	0.31
	101.53

This mineral is obviously a silicate. As a silicate may be regarded as a combination of basic and acidic oxides, the calcium oxide being present in the greatest amount, the metals will be calculated to calcium oxide. Disregarding the loss on ignition:

$$\frac{CaO}{FeO} = \frac{56.09}{71.85} \times 8.91 = 6.96\%\ CaO \equiv FeO,$$

$$\frac{CaO}{MnO} = \frac{56.09}{70.93} \times 10.20 = 8.07\%\ CaO \equiv MnO,$$

$$\frac{CaO}{ZnO} = \frac{56.09}{81.37} \times 10.15 = 7.00\%\ CaO \equiv ZnO,$$

$$\frac{CaO}{MgO} = \frac{56.09}{40.32} \times 3.61 = 5.02\%\ CaO \equiv MgO,$$

$$\underline{21.55\%\ CaO \text{ present},}$$

$$48.60\%\ CaO \text{ total}.$$

Calculating the Al_2O_3 into equivalent SiO_2, as it is probably present as an aluminate replacing silica:[1]

[1] On the supposition that the mineral contains the alumina combined as an aluminate and the silica as a silicate, then the aluminate can be represented as $3\ M''O \cdot Al_2O_3$ and the silicate as $M''O \cdot SiO_2$; whence it follows that as Al_2O_3 requires three $M''O$ and the SiO_2 one, hence $Al_2O_3 \equiv 3\ SiO_2$.

$$\frac{3\,SiO_2}{Al_2O_3} = \frac{3\,(60.3)}{102.2} \times 0.85 = 1.50\%\ SiO_2 \equiv Al_2O_3,$$

$$45.95\%\ SiO_2 \text{ present},$$

$$47.45\%\ SiO_2 \text{ total}.$$

$$SiO_2 = \frac{47.45}{60.3} = 0.788; \quad \frac{0.788}{0.788} = 1,$$

$$CaO = \frac{48.60}{56.09} = 0.866; \quad \frac{0.866}{0.788} = 1.1 = 1 \text{ approximately}.$$

The mineral is of the type $CaO \cdot SiO_2$ or $CaSiO_3$ or $R^{II}SiO_3$ in which R^{II} is chiefly Ca partially replaced by Mn, Zn, Fe^{II}, Mg, with a small amount of SiO_2 replaced by Al_2O_3, and is (Ca, Mn, Zn, Fe, Mg)SiO_3: (pyroxene).[1] This latter formula gives no indication as to the amounts of the metals present and does not show the alumina replacement.

[1] The sum of the percentages of SiO_2 and CaO total 96.05%. The mineral as analyzed shows 0.31% loss on ignition. Deducting this leaves the analysis footing up to 101.56 − 0.31 = 101.25%. Calculating the percentage on this basis gives (see p. 176):

$$\frac{47.45}{96.05} \times 101.25 = 50.02\%\ SiO_2,$$

$$\frac{48.60}{96.05} \times 101.25 = 51.23\%\ CaO,$$

$$101.25\%\ \text{total}.$$

Then

$$SiO_2 = \frac{50.02}{60.3} = 0.830; \quad \frac{0.830}{0.830} = 1,$$

$$CaO = \frac{51.23}{56.19} = 0.915; \quad \frac{0.915}{0.830} = 1.1 = 1 \text{ approximately},$$

and the ratio is as given before.

PROBLEMS

277. The atom of oxygen is 1.1431 times as heavy as the atom of nitrogen. (a) Taking the atomic weight of oxygen to be 16, what is the atomic weight of nitrogen? (b) If oxygen were 100, what is the atomic weight of nitrogen?

Ans. (a) 14.01.
(b) 87.56.

278. When oxygen is taken as 16, the atomic weight of iodine is 126.92 and hydrogen is 1.008. What is the atomic weight of iodine in a system taking hydrogen as unity? *Ans.* 125.91.

279. Erdmann and Marchand heated mercuric oxide:

$$2\,HgO = 2\,Hg + O_2.$$

From 113.3938 g. of mercuric oxide, 109.5308 g. of mercury were obtained. Calculate the atomic weight of mercury.

Ans. 200.17.

280. The atomic weight of lead was determined by Stas by converting lead into the nitrate: 100.00 g. of lead yielding 159.9703 g. of the nitrate. What is the atomic weight of lead from these data? *Ans.* 206.80.

281. Berzelius found that 2.265 g. of ferric oxide (Fe_2O_3) are formed from 1.586 g. of iron. Determine the atomic weight of iron from these data. *Ans.* 56.059.

282. Barium sulphate contains 58.85% barium, 13.73% sulphur and 27.41% oxygen. (*a*) What is the atomic weight of barium when oxygen is 16 and sulphur is 32.07? (*b*) What is the atomic weight of sulphur when barium is 137.41 and oxygen 16? *Ans.* (*a*) 137.41.
(*b*) 32.07.

283. The analysis of chromous chloride ($CrCl_2$) according to Pélegot is 57.50% chlorine and 42.50% chromium. What is the atomic weight of chromium? *Ans.* 52.419.

284. Lead sulphate on analysis yields 68.31% lead, 10.58% sulphur and 21.11% oxygen. What is the atomic weight of lead? *Ans.* 207.1.

285. According to Berzelius, litharge (PbO) contains 7.1724% oxygen. What is the atomic weight of lead? *Ans.* 207.08.

286. Calculate the atomic weight of silver from the following figures determined by Stas. 53.1958 g. of silver form 92.6042 g. of silver bromide. *Ans.* 107.88.

287. Dumas passed hydrogen gas over heated copper oxide. The copper oxide lost 59.789 g.; the water formed weighed 67.282 g. Calculate the atomic weight of hydrogen.

Ans. 1.0026.

288. Working with the reaction,

$$2\,Ag + Cl_2 = 2\,AgCl,$$

Stas found that 91.4620 g. of silver produced 121.4993 g. of silver chloride. Calculate the atomic weight of chlorine.

Ans. 35.428.

289. According to the reactions,

$$2\,AuCl_3 + 3\,SO_2 + 6\,H_2O = 2\,Au + 6\,HCl + 3\,H_2SO_4$$

$$3\,H_2SO_4 + 3\,BaCl_2 = 3\,BaSO_4 + 6\,HCl,$$

Levol found that 1000 parts of gold in the form of the chloride produce an amount of sulphuric acid that will precipitate 1728 parts of barium sulphate. Calculate the atomic weight of gold.

Ans. 202.64.

290. Chromic oxide (Cr_2O_3) contains 68.42% chromium and 31.58% oxygen. What is the atomic weight of chromium?

Ans. 52.00.

291. Erdmann and Marchand determined the atomic weight of mercury by heating the sulphide with copper,

$$HgS + Cu = CuS + Hg,$$

and found 177.1664 g. of mercuric sulphide gave 152.745 g. of mercury. Calculate the atomic weight of mercury.

Ans. 200.59.

292. The percentage composition of platinum chloride is

	Per cent
Platinum	57.92
Chlorine	42.08
	100.00

silver acetate (CH_3COOAg) yielded 18.612 g. silver. (*b*) 16.220 g. silver tartrate ($C_4H_4O_6Ag_2$) yielded 9.6175 g. silver. (*c*) 25.898 g. silver malate ($C_4H_4O_5Ag_2$) yielded 16.059 g. silver.

Ans. (*a*) 12.024.
(*b*) 12.02.
(*c*) 12.041.

303. Marignac made the following determinations for the calculation of the atomic weight of nitrogen: (*a*) From 314.894 g. of silver nitrate he obtained 200.000 g. of silver. (*b*) 14.1100 g. of silver nitrate required 6.1910 g. of potassium chloride for complete precipitation. (*c*) 10.339 g. of silver dissolved in nitric acid required 5.1200 g. of ammonium chloride for complete precipitation. Determine the atomic weight of nitrogen in each case and (*d*) the mean atomic weight of nitrogen from these determinations.

Ans. (*a*) 13.974.
(*b*) 14.055.
(*c*) 13.932.
(*d*) 13.987.

304. 3.000 g. of iodine dissolved in 90 g. of ethyl ether raised the boiling point 0.283° C. What is its molecular weight?

Ans. 254.

305. If 1.32 g. of formic acid dissolved in 100 g. of water lowers the freezing point 0.53° C., what is its molecular weight?

Ans. 46.1.

306. 10.000 g. of naphthalene dissolved in 100 g. of benzol lowers the freezing point 3.90° C. What is the molecular weight?

Ans. 128.

307. 1.67 g. of benzoic acid dissolved in 70 g. of ether raised the boiling point 0.422° C. Calculate the molecular weight.

Ans. 122.

308. 0.200 g. of alcohol dissolved in 100 g. of benzol lowered the freezing point 0.216° C. What is the molecular weight of the alcohol?

Ans. 46.3.

309. 1.000 g. of naphthalene dissolved in 50 g. of chloroform raised the boiling point 0.56° C. What is its molecular weight? *Ans.* 128.

310. Calculate the molecular weight of nitrosodiphenyl amine if 3.58 g. of the substance dissolved in 150 g. of benzol lowers the freezing point 0.601° C. *Ans.* 198.5.

311. Tartaric acid has two acidic hydrogen ions. When both these are replaced by silver the silver salt contains 59.31% silver. What is the molecular weight of tartaric acid assuming it contains no water of crystallization? *Ans.* 150.046.

312. Silver acetate has one replaceable hydrogen ion. 1.0000 g. of silver produces 1.5475 g. of silver acetate. What is the molecular weight of acetic acid? *Ans.* 60.073.

313. The silver salt of fumaric acid (dibasic) contains 65.43% silver. What is the molecular weight of fumaric acid? *Ans.* 116.016.

314. 2.0000 g. of the hydrochloro platinic acid salt of dimethyl aniline yield 0.5967 g. of platinum. What is the molecular weight of dimethyl aniline? *Ans.* 122.13.

315. 1.0000 g. of the hydrochloro platinic acid salt of pyridine yields 0.3436 g. of platinum on ignition. Calculate the molecular weight of pyridine. *Ans.* 79.08.

316. What is the molecular weight of ethyl amine if 3.0000 g. of the hydrochloro platinic acid salt yield 1.1708 g. of platinum on ignition? *Ans.* 45.10.

317. An analysis of arsenic pentoxide shows 65.2% arsenic and 34.8% oxygen. Its molecular weight is 230. What is the formula? *Ans.* As_2O_5.

318. Arsenic trichloride analyzes 41.4% arsenic and 58.6% chlorine. Its molecular weight is 181. What is the formula? *Ans.* $AsCl_3$.

319. Carbon trichloride shows a molecular weight of 237. Analysis shows it to contain 89.9% chlorine and 10.1% carbon. What is its molecular formula? *Ans.* C_2Cl_6.

220. Carbonil contains

	Per cent
Carbon	70.6
Hydrogen	4.2
Nitrogen	11.8
Oxygen	13.4

The molecular weight is 119. What is the formula?

Ans. C_7H_5NO.

221. Phenyl cyanide has a molecular weight of 103. Its composition is

	Per cent
Carbon	81.5
Hydrogen	4.9
Nitrogen	13.6

What is the formula? *Ans.* C_7H_5N.

222. Phenyl disulphide has a molecular weight of 218. Analysis shows 70.6% C_6H_5 and 29.4% sulphur. What is the formula? *Ans.* $(C_6H_5)_2S_2$.

223. What is the empiric formula of a compound analyzing:

	Per cent
Phosphorus	3.99
Bromine	82.30
Chlorine	13.70

Ans. PBr_4Cl_3.

224. What is the empiric formula of a compound of the composition:

	Per cent
Molybdenum	46.01
Oxygen	11.50
Chlorine	42.49

Ans. $Mo_2O_3Cl_6$.

225. If basic antimonyl sulphate has the composition

	Per cent
SbO	40.5
SO_4	14.2
Sb	35.5
OH	10.0

what is the formula? *Ans.* $(SbO)_2SO_4 \cdot Sb_2(OH)_4$.

326. Find the empiric formula of a compound of

	Per cent
Nickel	26.12
Hydrogen	0.90
Arsenic	44.51
Oxygen	28.48

Ans. $Ni_3H_6(AsO_3)_4$.

327. Find the empiric formula of a compound of

	Per cent
Chromic oxide (Cr_2O_3)	15.9
Sulphur trioxide (SO_3)	33.5
Ammonium oxide $(NH_4)_2O$	5.4
Hydrogen oxide (H_2O)	45.2

Ans. $Cr_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24\,H_2O$.

328. What is the formula of the following; lead being most accurately determined?

	Per cent
Lead	83.61
Sulphur	9.52
Chlorine	7.36

Ans. $Pb_4S_3Cl_2$.

329. Platinum is most accurately determined in the following. What is the formula?

	Per cent
Lithium	2.91
Platinum	36.84
Chlorine	40.10
Water	20.60

Ans. $Li_2PtCl_6 \cdot 6\,H_2O$.

330. Calculate the simplest formula, considering arsenic oxide as the most accurately determined, of

	Per cent
Arsenic oxide (As_2O_5)	37.91
Calcium oxide (CaO)	18.28
Ammonium oxide $(NH_4)_2O$	8.70
Water of crystallization	35.23

Ans. $CaNH_4AsO_4 \cdot 6\,H_2O$.

331. Calculate the empirical formula of the following substance, considering calcium as being most accurately determined.

	Per cent
Calcium	39.01
Phosphorus	19.85
Oxygen (by diff.)	41.14

Ans. $Ca_3P_2O_8$.

332. Find the formula of a substance analyzing

	Per cent
Potassium	11.47
Antimonyl (SbO)	40.80
Carbon	14.65
Hydrogen	1.19
Oxygen	29.08
Water of crystallization	2.60

considering the antimonyl most accurately determined.

Ans. $K_2(SbO)_2C_8H_8O_{12} \cdot H_2O$.

333. Given the following as the composition of Hypersthene, what is its formula?

	Per cent
SiO_2	54.20
FeO	21.70
MgO	24.10
	100.00

Ans. (Mg, Fe) SiO_3.

334. A sample of Smaltite examined by Hofmann gave the following analysis (disregard the Bi and S). What is its formula?

	Per cent
As	70.37
Co	13.95
Ni	1.79
Fe	11.71
Cu	1.39
S	0.66
Bi	0.01
	99.88

Ans. (Co,Ni,Fe,Cu) As_2.

335. A sample of Wad analyzed:

	Per cent
MnO_2	59.94
MnO	6.58
ZnO	21.70
Fe_2O_3	0.25
H_2O	11.58
	100.05

Disregarding the iron, what is the formula?

Ans. $2\ MnO_2 \cdot (Zn,Mn)\ O \cdot 2\ H_2O$.

336. What is the formula of a sample of Diallage analyzed by Von Rath, and found to be (disregarding the water):

	Per cent
SiO_2	53.60
Al_2O_3	1.99
FeO	8.95
MnO	0.28
MgO	13.08
CaO	21.06
H_2O	0.86
	99.82

Ans. $(Ca,Fe,Al,Mn,Mg)\ SiO_3$.

337. Show that the mineral analyzed below by Strüber (Gastaldite) approximates the formula $R_3Al_4Si_9O_{27}$.

	Per cent
SiO_2	58.55
Al_2O_3	21.40
FeO	9.04
MgO	3.92
CaO	2.03
Na_2O	4.77
	99.71

338. Deduce a formula for natrolite which was analyzed by Harrington with the following results:

	Per cent
SiO_2	47.09
Al_2O_3	26.99
Na_2O	16.46
K_2O	0.01
H_2O	9.80
	100.35

Ans. $Na_2O \cdot Al_2O_3 \cdot 3\,SiO_2 \cdot 2\,H_2O$.

339. What is the formula of Caberite which, according to Sachs, analyzes as follows:

	Per cent
As_2O_5	40.45
NiO	26.97
FeO	1.10
MgO	6.16
H_2O	25.26
	99.94

Ans. $(Ni,Fe,Mg)\,AsO_4 \cdot 8\,H_2O$.

340. Wolframite, according to Finlayson, gave on analysis the following, what is its formula?

	Per cent
WO_3	76.24
FeO	16.39
MnO	6.05
CaO	1.05
MgO	0.11
	99.84

Ans. $(Fe,Mn,Ca,Mg)WO_4$.

CHAPTER VIII

GRAVIMETRIC ANALYSIS

In a previous section, the amount of an element or radical obtainable from a given weight of a substance entering into a reaction was considered. It was postulated that the substances were pure, and only on this assumption are such calculations possible.

Direct Gravimetric Analysis. — Gravimetric analysis consists of weighing an element or compound of known composition and from this weight calculating the amount of a constituent present in the original substance. As gravimetric analyses are reported as percentages of constituents determined, it is necessary to know the weight of substance taken for analysis. Gravimetric analysis presupposes a knowledge of the elements or radicals present in the substance to be analyzed; in other words, it is preceded by a qualitative examination when the component elements or radicals are unknown.

As an example: A salt known to contain sodium and chlorine is to be examined as to its purity. One gram of the substance is weighed out and after proper precautions the chlorine is precipitated as silver chloride according to the reaction

$$NaCl + AgNO_3 = AgCl + NaNO_3,$$

the silver chloride in pure state being found to weigh 2.4382 g. The weight of chlorine present in the silver chloride is

$$\frac{\text{Cl}}{\text{AgCl}}^{1} = \frac{35.46}{143.34} \times 2.4382 = 0.6032 \text{ g. Cl},$$

and the percentage of chlorine is, one gram of substance being taken,

$$\frac{0.6032}{1.0000} \times 100 = 60.32\% \text{ Cl},$$

or in one equation

$$\frac{\text{Cl}}{\text{AgCl}} = \frac{35.46}{143.34} \times \frac{2.4382}{1.0000} \times 100 = 60.32\% \text{ Cl}.$$

The sodium of the sodium chloride is converted into pure sodium sulphate and weighed. The weight is found to be 1.2083 g. Then, as there are two atoms of sodium in sodium sulphate,

$$2 \text{ Na} \rightarrow \text{Na}_2\text{SO}_4,$$

the per cent of sodium present is,

$$\frac{2 \text{ Na}}{\text{Na}_2\text{SO}_4} = \frac{46.00}{142.07} \times \frac{1.2083}{1.0000} \times 100 = 39.12\% \text{ Na},$$

and the percentage accounted for is 60.32% + 39.12% = 99.44%. From these figures the compound is found to be NaCl. The impurities are present to the extent of 100.00% − 99.44% = 0.56%. A complete quantitative analysis would require the nature and the amount of these impurities. If it had been known in the beginning that the substance was sodium chloride, the amount of which in the sample is the end desired, the same could have

[1] An expression such as this is intended to mean that the fraction immediately following the equality sign has as its numerator and denominator the molecular weights of the symbols of the fraction. The equality sign cannot be interpreted as the equality sign of mathematics, but is meant only in this limited sense. The value of the fraction is the factor to use when AgCl is weighed, found or given and Cl is sought or required. See Chem. Ann., pp. 10–36.

been calculated from the amount of silver chloride obtained,

$$\frac{NaCl}{AgCl} = \frac{58.46}{143.34} \times \frac{2.4382}{1.0000} \times 100 = 99.44\% \text{ NaCl.}$$

In the same way the percentage of a radical present may be calculated. Suppose one gram of a substance known to be a sulphate yields 1.2318 g. of barium sulphate and that it is desired to know the per cent of sulphuric anhydride present. This is

$$\frac{SO_3}{BaSO_4} = \frac{80.07}{233.44} \times \frac{1.2318}{1.0000} \times 100 = 42.25\% \, SO_3.$$

When a reaction produces a gas, the volume may be measured and reduced to standard conditions and the weight of the same calculated. Suppose 0.5000 g. of calcite is treated with sulphuric acid,

$$CaCO_3 + H_2SO_4 = CaSO_4 + CO_2 + H_2O,$$

and that the carbon dioxide measured over water at 15° C. and 762 mm. is 118.2 cc. To determine the per cent of calcium carbonate, assuming that there are no other carbonates present: The volume of dry gas at standard (the tension of aqueous vapor at 15° C. being 12.73 mm.) is

$$\frac{273}{288} \times \frac{762 - 12.73}{760} \times 0.1182 = 0.11046 \text{ L. } CO_2,$$

the weight of which is

$$\frac{0.11046}{22.4} \times 44.00 = 0.2170 \text{ g. } CO_2.$$

This indicates the presence of

$$\frac{CaCO_3}{CO_2} = \frac{100.07}{44.00} \times \frac{0.2170}{0.5000} \times 100 = 98.70\% \, CaCO_3,$$

or better, proceeding to the final result by one expression,

$$\frac{273}{288}\times\frac{762-12.73}{760}\times\frac{0.1182}{22.4}\times\frac{100.07}{0.5000}\times 100 = 98.70\%\ CaCO_3.$$

Elimination of a Constituent from the Analysis. — Substances may contain water, water of crystallization, water mechanically held in the sample, oil and other impurities. When such substances are analyzed the amount of such material is determined; but when reporting, the analysis is often desired on the *dry basis*, or as if no such substances were present. In this case the constituents are reported with the same relative accuracy as was attained in the actual examination, excluding the substance it is desired to eliminate. A compound was analyzed and found to contain:

	Per cent
Moisture	1.47
Sodium oxide	57.42
Carbonic anhydride	40.65
	99.54

The analysis reported on the dry basis is

$$\frac{99.54}{99.54-1.47}\times 57.42 = 58.28\%\ Na_2O,$$

$$\frac{99.54}{99.54-1.47}\times 40.65 = 41.26\%\ CO_2,$$

$$99.54\%$$

Factor Weights. — In the calculation of percentage compositions, a ratio is usually employed, such ratios being known as factors. If, then, a weight of substance is taken for analysis numerically equal to the factor which must be employed, the percentage composition is ascertained directly and is numerically equal to the mass of the substance separated and weighed; due cognizance

being taken of the position of the decimal point. The factor for the determination of sulphur equivalent to barium sulphate is $\frac{S}{BaSO_4} = \frac{32.07}{233.44} = 0.13738$. Then if X units of mass of barium sulphate are produced from a quantity of material numerically equal to the factor 0.13738, the percentage of sulphur is

$$0.13738 \times \frac{X}{0.13738} \times 100 = 100\,X.$$

The per cent of sulphur in the sample is given by the weight of the barium sulphate produced, the decimal point in this case being moved two points to the right. Weights numerically equal to the factor or to some simple multiple or submultiple of the factor which is to be employed are called factor weights.

Indirect Analysis. — Of indirect analysis there are so many different cases that all will not be treated individually. A few types will be considered.

Case I. — In which an equivalent amount of some other element or radical is determined. In the reaction

$$As_2O_3 + 2\,H_2O + 2\,I_2 = 4\,HI + As_2O_5,$$

the amounts of iodine necessary for the oxidation of arsenious oxide to arsenic oxide being known, the amount of arsenious oxide or arsenic present is readily calculated. 0.1014 g. of a sample containing arsenious oxide required 0.2582 g. of iodine to oxidize to arsenic oxide. The percentage of arsenious oxide is

$$\frac{As_2O_3}{4\,I} = \frac{198.92}{507.68} \times \frac{0.2582}{0.1014} \times 100 = 99.27\%\ As_2O_3,$$

or if the percentage of the metal arsenic had been required,

$$\frac{As_2}{4\,I} = \frac{149.92}{507.68} \times \frac{0.2582}{0.1014} \times 100 = 75.20\%\ As.$$

Case II. — Simple cases in which mixtures are weighed and an element or radical in it subsequently determined. Given the following:

Amount of substance taken....	5.0000 g.
Which yields.....	1.0000 g. $Al_2O_3 + Fe_2O_3$
Which in turn yields.....	0.1795 g. Fe

to calculate the percentages of iron and aluminum in the sample. The percentage of iron is

$$\frac{0.1795}{5.0000} \times 100 = 3.59\%\ Fe.$$

The amount of Fe_2O_3 equivalent to 0.1795 g. of Fe is

$$\frac{Fe_2O_3}{2\,Fe} = \frac{159.68}{111.68} \times 0.1795 = 0.2566\ g.\ Fe_2O_3,$$

then the amount of Al_2O_3 which was present in 1.0000 g. of the mixed oxides must have been 1.000 − 0.2566 = 0.7434 g. Al_2O_3. The per cent of aluminum is

$$\frac{2\,Al}{Al_2O_3} = \frac{54.2}{102.2} \times \frac{0.7434}{5.0000} \times 100 = 7.89\%\ Al.$$

Case III. — Simple cases in which mixtures are weighed and the mixture subsequently converted into a single compound. Given:

Weight of substance taken.....	1.5000 g.
Weight of mixture of AgBr + AgCl obtained..	1.1060 g.
Weight of AgCl produced from the mixture[1]...	0.9563 g.

to calculate the percentages of bromine and chlorine present in the original sample.

[1] The whole mixture AgCl + AgBr is converted into AgCl:

$$x\,AgCl + y\,AgBr + \frac{y}{2}\,Cl_2 = (x + y)\,AgCl + \frac{y}{2}\,Br_2.$$

It is evident that an atom of chlorine has replaced an atom of bromine causing a loss of weight of 1.1060 − 0.9563 = 0.1497 g. The loss in molecular weight corresponding to this is AgBr − AgCl = 187.80 − 143.34 = 44.46, or what amounts to the same, the difference of the atomic weights of bromine and chlorine: 79.92 − 35.46 = 44.46. The amount of bromine present which would cause this loss of weight is

$$\frac{\text{Br}}{\text{Br} - \text{Cl}} = \frac{79.92}{44.46} \times 0.1497 = 0.2691 \text{ g. Br},$$

and the per cent of bromine in the substance taken is

$$\frac{0.2691}{1.5000} \times 100 = 17.94\% \text{ Br}.$$

The amount of silver bromide equivalent to the bromine, *i.e.*, the amount that must have been present in the mixture, is

$$\frac{\text{AgBr}}{\text{Br}} = \frac{187.80}{79.92} \times 0.2691 = 0.6323 \text{ g. AgBr},$$

or what amounts to the same,

$$\frac{\text{AgBr}}{\text{Br} - \text{Cl}} = \frac{187.80}{44.46} \times 0.1497 = 0.6323 \text{ g. AgBr}.$$

The weight of silver chloride present in the mixture is 1.1060 − 0.6323 = 0.4737 g. The per cent of chlorine in the substance taken is

$$\frac{\text{Cl}}{\text{AgCl}} = \frac{35.46}{143.34} \times \frac{0.4737}{1.5000} \times 100 = 7.81\% \text{ Cl}.$$

[1] The fraction $\frac{\text{Br}}{\text{Br} - \text{Cl}}$ is meant to show that the fraction just after the equality sign is made up of numbers equal to the molecular weights of the elements symbolized and that the operation has been carried out. In this case,

$$\frac{\text{Br}}{\text{Br} - \text{Cl}} = \frac{70.92}{70.92 - 36.46} = \frac{70.92}{44.64}.$$

To make this calculation algebraically, let

x = weight of silver chloride present in the mixture,
y = weight of silver bromide present in the mixture,
a = weight of mixed silver salts,
b = weight of mixed silver salts converted into silver chloride,
f = factor for the conversion of $AgBr \rightarrow AgCl$

$$= \frac{AgCl}{AgBr} = \frac{143.34}{187.80} = 0.76325.$$

Then

$$x + y = a,$$
$$x + fy = b,$$

eliminating x by subtracting and solving for y,

$$y = \frac{a - b}{1 - f},$$

substituting the value of f,

$$y = \frac{a - b}{1 - 0.76325} = \frac{a - b}{0.23675} = 4.2239\,(a - b),$$
$$x = a - y.$$

Applying to the problem given:

$$\begin{aligned} x + \quad\quad y &= 1.1060 \\ x + 0.76325\,y &= 0.9563 \\ \hline y &= \frac{1.1060 - 0.9563}{1 - 0.76325} \\ &= 0.6323 \text{ g. AgBr.} \end{aligned}$$

Knowing that the reciprocal of $1 - 0.76235$ is 4.2239, it is easier to proceed immediately to the result:

$y = 4.2239\,(1.1060 - 0.9563) = 0.6323$ g. AgBr,
$x = 1.1060 - 0.6323 = 0.4737$ g. AgCl,

and the percentages of chlorine and bromine in the sample taken are:

$$\frac{\text{Br}}{\text{AgBr}} = \frac{79.92}{187.80} \times \frac{0.6323}{1.5000} \times 100 = 17.94\%\ \text{Br},$$

$$\frac{\text{Cl}}{\text{AgCl}} = \frac{35.46}{143.34} \times \frac{0.4737}{1.5000} \times 100 = 7.81\%\ \text{Cl}.$$

Instead of calculating the chlorine and bromine from the weights of the silver chloride and silver bromide, the amounts of chlorine and bromine can be determined directly, as, for instance, the factor of $\frac{\text{Br}}{\text{AgBr}}$ being $\frac{79.92}{187.80}$, the weight of bromine (z) is

$$z = \frac{79.92}{187.80} \times 4.2239\,(a - b)$$
$$= 1.7975\,(a - b).$$

Multiplying factors are given in chemists' handbooks, the above being a method by which they are calculated.[1] To calculate the factor for the chlorine:

$$x + fy = b,$$
$$\underline{x + y = a,}$$
$$\therefore\ x = \frac{b - fa}{1 - f};$$

substituting the values of f,

$$x = \frac{b - 0.76325a}{0.23675} = 4.2239(b - 0.76325a) = 4.2239b - 3.2239a.$$

The factor to determine chlorine in silver chloride being

$$\frac{\text{Cl}}{\text{AgCl}} = \frac{35.46}{143.34} = 0.24738,$$

then, if w is the weight of chlorine,

$$w = 0.24738\,(4.2239\,b - 3.2239\,a) = 1.0449\,b - 0.79754\,a.$$

[1] This same factor could have been obtained in the method preceding the algebraic method: $\frac{\text{Br}}{\text{Br} - \text{Cl}} = \frac{79.92}{44.46} = 1.7975.$

Case IV. — Complex cases in which a known weight of the mixture is subsequently converted into a single element or a radical. Given:

Weight of KCl + NaCl in mixture	1.0000 g.
Weight of Cl in the mixture subsequently determined	0.5411 g.

it is required to determine the weights of sodium chloride and potassium chloride present in the mixture. Several methods will be given.

Method (a). — If the mixture of KCl + NaCl had been pure NaCl the amount of chlorine would be

$$\frac{\text{Cl}}{\text{NaCl}} = \frac{35.46}{58.46} \times 1.0000 = 0.60657 \text{ g. Cl};$$

if it had been pure KCl the amount of chlorine would be

$$\frac{\text{Cl}}{\text{KCl}} = \frac{35.46}{74.56} \times 1.0000 = 0.47559 \text{ g. Cl.}$$

The difference between the chlorine content if the mixture had been pure sodium chloride or pure potassium chloride is 0.60657 − 0.47559 = 0.13098 g. The observed difference due to the presence of potassium chloride in the mixture is 0.60657 − 0.5411 = 0.06547 g. The amount of potassium chloride in the mixture must be, therefore,

$$\frac{0.06547}{0.13098} \times 1.0000 = 0.4999 \text{ g. KCl.}$$

Then the weight of sodium chloride present in the mixture is 1.0000 − 0.4999 = 0.5001 g. Knowing the amounts of sodium chloride and potassium chloride, also the weight taken, the percentages are calculated in the usual way.

Method (b). — If the mixture were pure potassium chloride, the weight of the mixture equivalent to 0.5411 g. of chlorine is

$$\frac{\text{KCl}}{\text{Cl}} = \frac{74.56}{35.46} \times 0.5411 = 1.1378 \text{ g.}$$

1.1378 − 1.0000 = 0.1378 g., excess due to the presence of sodium chloride. The amount of sodium chloride corresponding to this difference is

$$\frac{\text{NaCl}}{\text{KCl} - \text{NaCl}} = \frac{58.46}{74.56 - 58.46} = \frac{58.46}{16.10} \times 0.1378$$
$$= 0.5004 \text{ g. NaCl},$$
$$1.0000 - 0.5004 = 0.4996 \text{ g. KCl}.$$

Method (*c*). — Let

x = weight of KCl in mixture,
y = weight of NaCl in mixture,
a = weight of mixture,
b = weight of Cl in mixture,
f = factor to determine the amount of Cl in KCl = 0.47559,
q = factor to determine the amount of Cl in NaCl = 0.60657.

Then

$$x + y = a,$$
$$fx + qy = b.$$

Substituting the values for the particular problem under consideration:

$$\begin{array}{rr} x+ & y=1.0000 \\ \underline{0.47559\,x+0.60657\,y=0.5411} & \\ x=0.4999=\text{g. KCl} & \\ y=1.0000-0.4999=0.5001=\text{g. NaCl}. & \end{array}$$

Another problem will be cited but slightly different from the foregoing. A sample containing potassium iodide and potassium bromide is to be examined for percentage composition. One gram of the sample yields 1.5370 g. of mixed silver bromide and silver iodide. This mixture is now converted into silver chloride and weighs 1.1191 g. Although this latter compound contains none of the elements sought, these can be readily calculated.

If the mixture weighed had been pure silver iodide, the amount of chloride would have been

$$\frac{\text{AgCl}}{\text{AgI}} = \frac{143.34}{234.80} \times 1.5370 = 0.9383 \text{ g. AgCl.}$$

If the mixture had been pure silver bromide, the amount of silver chloride would have been

$$\frac{\text{AgCl}}{\text{AgBr}} = \frac{143.34}{187.80} \times 1.5370 = 1.1731 \text{ g. AgCl.}$$

1.1191 − 0.9383 = 0.1808 g., excess of silver chloride beyond what it would be if it were pure silver iodide, the excess being due to the presence of silver bromide. 1.1731 − 0.9383 = 0.2348 g., the difference in weight between what the silver chloride would weigh if derived from pure silver iodide or pure silver bromide. The weight of silver bromide present amounts to

$$\frac{0.1808}{0.2348} \times 1.5370 = 1.1835 \text{ g. AgBr,}$$

and

$$1.5370 - 1.1835 = 0.3535 \text{ g. AgI.}$$

The percentages of the potassium bromide and potassium iodide in the original sample are:

$$\frac{\text{KBr}}{\text{AgBr}} = \frac{119.02}{187.80} \times \frac{1.1835}{1.0000} \times 100 = 75.00\% \text{ KBr,}$$

$$\frac{\text{KI}}{\text{AgI}} = \frac{166.02}{234.80} \times \frac{0.3535}{1.0000} \times 100 = 25.00\% \text{ KI.}$$

Algebraically, the factors being

$$\text{AgI} \rightarrow \text{AgCl} = \frac{\text{AgCl}}{\text{AgI}} = 0.61047,$$

$$\text{AgBr} \rightarrow \text{AgCl} = \frac{\text{AgCl}}{\text{AgBr}} = 0.76325;$$

then, if

x = weight of AgBr,
y = weight of AgI,

$$x + y = 1.5370,$$
$$0.76325\,x + 0.61047\,y = 1.1191.$$

Solving,

$$x = 1.1835 \text{ g. AgBr},$$
$$y = 1.5370 - 1.1835 = 0.3535 \text{ g. AgI}.$$

The percentages are calculated as given before.

The calculation of a factor in this case is as follows: let

x = grams AgBr present in the mixed salt,
y = grams AgI present in the mixed salt,
a = grams mixed salt,
b = grams AgCl obtained from the mixed salt,
f = factor for the conversion: AgBr $\rightarrow$ AgCl,

$$= \frac{\text{AgCl}}{\text{AgBr}} = \frac{143.34}{187.80} = 0.76325,$$

k = factor for the conversion: AgI $\rightarrow$ AgCl;

$$= \frac{\text{AgCl}}{\text{AgI}} = \frac{143.34}{234.80} = 0.61047.$$

Then

$$x + y = a,$$
$$fx + ky = b,$$
$$y = \frac{fa - b}{f - k}.$$

Substituting the values of f and k,

$$y = 4.9959\,a - 6.5454\,b.$$

If it is desired to know the amount of iodine in the mixed salts, the factor of iodine equivalent to silver iodide being $\frac{\text{I}}{\text{AgI}} = \frac{126.92}{234.80} = 0.54054$, then if q is the weight of iodine present,

$$q = 0.54054\,(4.9959\,a - 6.5454\,b)$$
$$= 2.7005\,a - 3.5381\,b.$$

The above is a general method.[1] Having the value of y for any mixed salt of silver bromide and silver iodide, a factor such as q may be calculated for any desired element, radical or compound known to be present in the original sample.

Case V. — In which a mixture containing two salts having an element or radical in common is converted into another mixture, also containing an element or radical in common. Given, one gram of a mixture of sodium chloride and potassium chloride; the mixture being converted by treatment with sulphuric acid into a mixture of sodium sulphate and potassium sulphate, the weight of this latter mixture being 1.18600 g. It is required to calculate the weights of sodium chloride and potassium chloride present in the original mixture. If the substance had been pure sodium chloride, the weight of sodium sulphate obtainable would be

$$\frac{Na_2SO_4}{2\,NaCl} = \frac{142.07}{116.92} \times 1.00000 = 1.21510\,\text{g. } Na_2SO_4.$$

If it had been pure potassium chloride, the weight obtained from one gram would be

$$\frac{K_2SO_4}{2\,KCl} = \frac{174.27}{149.12} \times 1.00000 = 1.16866\,\text{g. } K_2SO_4.$$

The difference between these weights is

$$1.21510 - 1.16866 = 0.04644\,\text{g.}$$

The difference between the weight found and the weight which would have been obtained if the substance had been pure sodium chloride is

$$1.18600 - 1.16866 = 0.01734\,\text{g.}$$

[1] For a tabulation of indirect factors, see Chem. Ann., pp. 37–38.

Therefore, the amount of sodium chloride present in the mixture of chlorides is

$$\frac{0.01734}{0.04644} \times 1.00000 = 0.37338 \text{ g. NaCl.}$$

By the same line of reasoning, the potassium chloride is

$$1.21510 - 1.18600 = 0.02910.$$

$$\frac{0.02910}{0.04644} \times 1.00000 = 0.62662 \text{ g. KCl,}$$

or, by difference,

$$1.00000 - 0.37388 = 0.62662 \text{ g. KCl.}$$

To calculate algebraically, let x = weight of NaCl, then $1 - x$ = weight of KCl.

$$m = \text{factor}\frac{Na_2SO_4}{2\ NaCl} = 1.2151044,$$

$$n = \text{factor}\frac{K_2SO_4}{2\ KCl} = 1.168656.$$

$$1.215104\,x + 1.168656\,(1 - x) = 1.18600,$$
$$1.215104\,x + 1.168656 - 1.168656\,x = 1.18600,$$
$$0.046448\,x = 0.01734,$$
$$x = \frac{0.01734}{0.046448} = 0.37338 \text{ g. NaCl.}$$
$$1.00000 - 0.37338 = 0.62662 \text{ g. KCl.}$$

To calculate the factor, let

x = weight of sodium chloride,
y = weight of potassium chloride,
a = weight of mixed sulphates,
b = weight of mixed chlorides,

$$m = \text{factor}\frac{Na_2SO_4}{2\ NaCl} = 1.2151044,$$

$$n = \text{factor}\frac{K_2SO_4}{2\ KCl} = 1.168656.$$

$$1.215104\,x + 1.168656\,(b - x) = a,$$
$$1.215104\,x + 1.168656\,b - 1.168656\,x = a,$$
$$0.046448\,x = a - 1.168656\,b,$$

$$x = \frac{a - 1.168656\,b}{0.046448} = 21.5293\,(a - 1.168656\,b)$$
$$= 21.5293\,a - 25.1604\,b.$$

$$1.168656\,y + 1.215104\,(b - y) = a,$$
$$1.168656\,y + 1.215104\,b - 1.215104\,y = a,$$
$$-0.046448\,y = -1.215104\,b + a,$$

$$y = \frac{1.215104\,b - a}{0.046448} = 21.5293\,(1.215104\,b - a)$$
$$= 26.1604\,b - 21.5293\,a.$$

To calculate this factor in another manner, let

x = weight of sodium chloride,
y = weight of potassium chloride,
a = weight of mixed sulphates,
b = weight of mixed chlorides,

$$m = \text{factor}\frac{Na_2SO_4}{2\,NaCl} = 1.2151044,$$

$$n = \text{factor}\frac{K_2SO_4}{2\,KCl} = 1.168656.$$

Factor for sodium chloride:

$$x + y = b,$$
$$mx + ny = a,$$
$$nx + ny = nb,$$
$$mx + ny = a,$$
$$(m - n)\,x = a - nb,$$
$$x = \frac{a - nb}{m - n},$$
$$x = \frac{1}{m - n}\,a - \frac{n}{m - n}\,b.$$

Factor for potassium chloride:

$$x + y = b,$$
$$mx + ny = a,$$
$$mx + my = mb,$$
$$mx + ny = a,$$
$$(m - n)\,y = mb - a,$$
$$y = \frac{mb - a}{m - n},$$
$$y = \frac{m}{m - n}\,b - \frac{1}{m - n}\,a.$$

Substituting the values of m and n,

$$x = \frac{1}{0.046448}a - \frac{1.16866}{0.046448}b. \qquad y = \frac{1.215104}{0.046448}a - \frac{1}{0.046448}b,$$

$$x = 21.5293\,a - 25.1604\,b. \qquad y = 26.1604\,b - 21.5293\,a.$$

An inspection of these factors shows that an error made in weighing the mixed chlorides or mixed sulphates is multiplied more than twenty times in calculating the results. This should serve as a warning against using an indirect method of analysis when a direct method may be made to serve. Such methods of indirect analysis, beautiful as they may appear on paper, are to be avoided, except, possibly, in those cases in which the multiplying factor is small. The errors are less when approximately equal weights of the two substances are present. They may become very large when one of the substances is present to a much larger extent than the other.

A table of calculations is given on page 190 showing the errors introduced by only one milligram error in weighing the mixed chlorides or sulphates. From an inspection of this table, it is clear that this particular method, at least, is little short of useless, except in exceptional cases and when the weights of the two chlorides are about equal.

	Theoretical mixture		Weight of mixed chlorides: g. (*b*)	Weight of mixed sulphates: g. (*a*)	Indicated percentage		Percentage error		Percentage error, on amount present	
	NaCl g.	KCl g.			NaCl	KCl	NaCl	KCl	NaCl	KCl
Theoretical	0.50000	0.50000	1.00000	1.19188	50.00	50.00	....	....	.....	.....
Error of +1 mgr. in weighing mixed chlorides	0.50000	0.50000	1.00100	1.19188	47.48	52.62	−2.52	+2.62	− 5.04	+ 5.24
Error of +1 mgr. in weighing mixed sulphates	0.50000	0.50000	1.00000	1.19288	52.15	47.85	+2.15	−2.15	+ 4.30	− 4.30
Theoretical	0.90000	0.10000	1.00000	1.21046	90.00	10.00	....	....	.....	.....
Error of +1 mgr. in weighing mixed chlorides	0.90000	0.10000	1.00100	1.21046	87.48	12.62	−2.52	+2.62	− 2.80	+26.20
Error of +1 mgr. in weighing mixed sulphates	0.90000	0.10000	1.00000	1.21146	92.15	7.85	+2.15	−2.15	+ 2.39	−21.50
Theoretical	0.10000	0.90000	1.00000	1.17330	10.00	90.00	....	....	.....	.....
Error of +1 mgr. in weighing mixed chlorides	0.10000	0.90000	1.00100	1.17330	7.48	92.62	−2.52	+2.62	−25.20	+ 2.91
Error of +1 mgr. in weighing mixed sulphates	0.10000	0.90000	1.00000	1.17430	12.15	87.85	+2.15	−2.15	+21.50	− 2.39

Mixture of Sulphuric Acid and Sulphuric Anhydride (Oleum). — Another case of mixtures is the acids and their anhydrides. The commonest of these is "oleum" or fuming sulphuric acid, being a mixture of H_2SO_4 and varying amounts of SO_3.[1] In commerce an oleum is spoken of as being 30% oleum, for example, when it contains 30% by weight of free sulphur trioxide, the remainder being sulphuric acid, the per cent of *free* sulphur trioxide serving to designate the per cent oleum.

Suppose it is required to know the *total* per cent of sulphur trioxide in a sample of oleum. Let

x = per cent oleum, *i.e.*, the per cent uncombined SO_3,

$100 - x$ = per cent sulphuric acid,

then as the factor $\frac{SO_3}{H_2SO_4} = \frac{80.07}{98.09} = 0.8163$, if y is the per cent total SO_3,

$$y = 0.8163\,(100 - x) + x.$$

Or being given the per cent total SO_3, to find the per cent uncombined SO_3, *i.e.*, the per cent oleum, from the equation above is obtained

$$x = 5.4436\,(y - 81.63).^2$$

Examples. — (*a*) What is the percentage total SO_3 in 30% oleum? (*b*) A sample of oleum analyzes 85.31% SO_3. What per cent oleum is it?

(*a*) $y = 0.8163\,(100 - 30) + 30$

$= 87.14\%\ SO_3$.

(*b*) $x = 5.4436\,(85.31 - 81.63)$

$= 20.03\%$ oleum.

[1] As SO_3 has a great affinity for water, oleum can contain no H_2O as water.

[2] For a table of percentages of oleum corresponding to percentages total SO_3, see Chem. Ann., pp. 397–398. This table may be calculated by the method given.

PROBLEMS

341. 0.2017 g. of a substance containing potassium yields 0.7092 g. of potassium platinic chloride. What is the per cent of potassium? *Ans.* 56.56%.

342. A substance known to be largely $NaHSO_4 \cdot H_2O$ is examined as to its purity; 0.3062 g. of it produces 0.5093 g. of barium sulphate. What is the per cent of acid sodium sulphate? *Ans.* 98.40%.

343. Calcium fluoride was analyzed by precipitating the fluorine as barium silicofluoride ($BaSiF_6$) and the calcium was estimated as the oxide. 0.5042 g. of the fluoride gave 0.6002 g. of barium silicofluoride and 0.3630 g. of calcium oxide. What is the per cent composition according to these figures?

Ans. 48.52% F.
51.45% Ca.

344. A substance is suspected of being phosphorus pentoxide (P_2O_5). 0.5043 g. of the substance dissolved in water gave 0.7835 g. of magnesium pyrophosphate ($Mg_2P_2O_7$). Was the substance phosphorus pentoxide? *Ans.* Yes, 99.10%.

345. A sample of a substance is known to be an oxide of arsenic. 0.2504 g. gave 0.3912 g. of magnesium pyroarsenate ($Mg_2As_2O_7$). Is the substance arsenic oxide (As_2O_5) or arsenious oxide (As_2O_3)? *Ans.* 99.57% As_2O_3.

346. A sample containing barium, chlorine and water of crystallization was analyzed and the following figures obtained:

Weight of sample taken	1.0000 g.
Weight after heating (water driven off)	0.8522 g.
Weight of barium sulphate obtained	0.9594 g.
Weight of silver chloride obtained	1.1735 g.

(*a*) Calculate the percentage of each constituent; (*b*) the formula of the substance and (*c*) the per cent errors on the assumption that the sample was pure.

Ans. (*a*) 14.78% H_2O; 56.46% Ba; 29.03% Cl.
(*b*) $BaCl_2 \cdot 2\,H_2O$.
(*c*) H_2O, + 0.03%; Cl, ± 0; Ba, + 0.23%.

347. Potassium chlorate was analyzed as follows: the oxygen determined by loss of weight on heating; one gram lost 0.3900 g. The chlorine determined by precipitation as silver chloride; one gram producing 1.1594 g. silver chloride. The potassium was weighed as potassium sulphate; one gram giving 0.7098 g. of potassium sulphate. (*a*) Find the per cent composition from these figures and (*b*) the formula.

Ans. (*a*) 39.00% O.
28.68% Cl.
31.85% K.
(*b*) $KClO_3$.

348. A sample is analyzed for sodium oxide (Na_2O) and carbonic anhydride (CO_2). 1.3417 g. of sodium sulphate are obtained from one gram of substance. The same amount produces 229 cc. of carbonic anhydride measured moist at 17° C. and 757 mm. (*a*) What per cent of these constituents are present and (*b*) what is the formula of the compound? (Ten. aq. vapor at 17° C. = 14.45 mm.) *Ans.* (*a*) 58.55% Na_2O.
41.37% CO_2.
(*b*) Na_2CO_3.

349. One gram of a solution of hydrogen dioxide is boiled liberating oxygen

$$2\,H_2O_2 = 2\,H_2O + O_2.$$

25.7 cc. of oxygen are produced measured moist at 758 mm. and 15° C. What is the per cent of hydrogen dioxide in the solution? (Ten. aq. vapor at 15° C. = 12.73 mm.) *Ans.* 3.69%.

350. A coal analyzes as follows:

	Per cent
Volatile combustible matter including sulphur	18.10
Fixed carbon	74.52
Sulphur	0.60
Ash	6.65
Water	0.73
	100.60

What are these percentages on the dry basis?

Ans. 18.23%; 75.06%; 0.61%; 6.70%.

351. A coke analyzes:

	Per cent
Volatile combustible matter	1.58
Fixed carbon	88.87
Sulphur	1.18
Ash	8.99
Water	1.92
	102.54

What is its composition on the dry basis?

Ans. 1.61%; 90.56%; 1.20%; 9.16%.

352. The extracted pigment of a paint analyzes:

	Per cent
White lead	30.42
Zinc oxide	61.52
Asbestine	7.23
Unextracted oil	1.06
	100.23

Calculate the percentages present if all the oil had been extracted.

Ans. 30.74%; 62.18%; 7.31%.

353. A sample of phosphate rock analyzes:

	Per cent
Calcium phosphate	96.02
Ferric oxide	1.13
Aluminum oxide	0.60
Insoluble	1.24
Moisture	0.73
	99.90

Calculate the percentages on the dry basis.

Ans. 96.91%; 1.14%; 0.60%; 1.25%.

354. On the dry basis, a sample of coal analyzes:

	Per cent
Volatile combustible	21.06
Fixed carbon	71.80
Ash	7.14
	100.00

If the moisture present in the coal was 2.49%, what is the analysis on the wet basis?

Ans. 20.54%
70.01%
6.96%
2.49%
100.00%

355. A sample of coal was dried at 70° C., at which temperature a loss of 6.03% water was obtained. The partially dried sample was analyzed and showed:

	Per cent
Volatile material	8.23
Fixed carbon	65.90
Ash	23.80
Moisture	2.07
	100.00

What are the percentages on the original sample?

Ans. 7.73%
61.93%
22.36%
7.78%
100.00%

356. The pigment of a certain paint has the composition:

	Per cent
(*a*) White lead	33.30
(*b*) Zinc oxide	66.70
	100.00

The vehicle of this paint consists of

	Per cent
(*c*) Linseed oil	32.40
(*d*) Japan dryer	13.60
(*e*) Asphaltum spirits	54.00
	100.00

The pigment and vehicle are mixed to form the paint in the proportions:

	Per cent
Pigment	63.00
Vehicle	37.00
	100.00

Calculate the percentage composition of this paint.

Ans. (*a*) 20.98%.
(*b*) 42.02%.
(*c*) 11.99%.
(*d*) 5.03%.
(*e*) 19.98%.

strontium sulphate are obtained. What are the percentages of calcium oxide and strontium oxide? *Ans.* 5.40% SrO.
4.01% CaO.

368. Calculate the percentages of sodium and potassium, given the following data:

Weight of substance taken	2.0000 g.
Weight of NaCl + KCl obtained	0.6437 g.
Weight of K_2PtCl_6 obtained from mixture	0.6514 g.

Ans. 5.24% K.
8.92% Na.

369. A substance contains sodium and potassium. It gives 36.42% of mixed sodium and potassium sulphates. From the mixed sulphates is obtained a weight of potassium platinic chloride (K_2PtCl_6) that amounts to 47.20% of the weight of sample taken. What are the percentages of sodium and potassium oxide? *Ans.* 9.15% K_2O.
8.51% Na_2O.

370. 1.5000 g. of a substance containing bromine and chlorine yield 1.0000 g. of mixed silver chloride and silver bromide. The mixture is treated with chlorine, converting the silver bromide into silver chloride, the loss of weight due to this change being 0.1367 g. What are the percentages of chlorine and bromine? *Ans.* 16.38% Br.
6.97% Cl.

371. What are the percentages of chlorine and iodine in a substance, 2.0000 g. of which yield 1.5230 g. of mixed silver chloride and iodide, which mixture when converted into the chloride yields 1.1090 g. of silver chloride? *Ans.* 28.73% I.
15.69% Cl.

372. A sample composed of potassium chlorate ($KClO_3$) and potassium bromate ($KBrO_3$) is examined by the indirect method. One gram was taken from which 1.0474 g. of mixed silver chloride and bromide were obtained. From this mixture 1.0138 g. of silver chloride were obtained. What are the percentages

of potassium chlorate and potassium bromate in the original sample? *Ans.* 12.62% $KBrO_3$.
77.42% $KClO_3$.

373. If

x = weight of AgCl present,
y = weight of AgI present,
a = weight of mixture of AgCl + AgI,
b = weight of AgCl obtained from (a):

(a) Calculate the factor which multiplying $(a - b)$ gives the weight of silver iodide, and (b) the factor that multiplying $(a - b)$ gives the weight of iodine. *Ans.* (a) 2.5672 $(a - b)$.
(b) 1.3877 $(a - b)$.

374. Taking the factors of problem 373, (a) what are the amounts of silver chloride and silver iodide when the mixed salts weigh 1.8320 g. and the mixed salts converted into the chloride weigh 1.5232 g.? (b) What is the weight of iodine present? *Ans.* (a) 0.7928 g. AgI.
1.0392 g. AgCl.
(b) 0.4285 g. I.

375. What is the factor to be used which multiplying the loss of weight caused by converting a mixture of silver chloride and silver bromide into silver chloride will give the amount of bromine present? *Ans.* 1.7976.

376. What is the factor to be used which multiplying the loss of weight caused by converting a mixture of silver chloride and silver iodide into silver chloride will give the weight of iodine? *Ans.* 1.3877.

377. One gram of a mixture of silver iodide and silver bromide is converted into silver chloride, yielding 0.6487 g. of the same. What are the weights of iodine and bromine in the mixture? *Ans.* 0.1065 g. Br.
0.4053 g. I.

378. 1.0721 g. of a mixture of calcium carbonate and strontium carbonate yield 1.4217 g. of a mixture of strontium sul-

phate and calcium sulphate. How much calcium carbonate and strontium carbonate were contained in the mixture?

Ans. 0.7574 g. $CaCO_3$.
0.3148 g. $SrCO_3$.

379. 0.5541 g. of a mixture of potassium iodide and bromide yield 0.3396 g. of potassium sulphate. How much iodine and bromine in the mixture? *Ans.* 0.2436 g. I.
0.1581 g. Br.

380. A mixture of potassium sulphate and sodium sulphate weighs 1.4304 g. From this mixture 2.1364 g. of barium sulphate are obtained. (*a*) What are the weights of potassium sulphate and sodium sulphate in the mixture? (*b*) If 1.5000 g. of the substance were taken from which this mixture was obtained, what are percentages of sodium and potassium in the original sample?

Ans. (*a*) 0.7257 g. Na_2SO_4.
0.7047 g. K_2SO_4.
(*b*) 15.67% Na.
21.08% K.

381. Calculate the factors that applied to the previous problem (380) will give the weights of potassium and sodium. These are to be multiplying factors.

Ans. $K = 2.4278\,a - 1.4775\,b$,
$Na = 1.0662\,b - 1.4280\,a$.

382. One gram of a mixture consisting of silver chloride and silver bromide is found to contain 0.6635 g. of silver. (*a*) How much bromine and (*b*) how much chlorine does it contain?

Ans. (*a*) 0.2128 g. Br.
(*b*) 0.1237 g. Cl.

383. Calculate factors which when multiplying the weight of the mixed salt of problem 382 and the weight of silver obtained from the mixture will give the weights of bromine and chlorine present. *Ans.* $Cl = 1.3884\,b - 0.79753\,a$.
$Br = 1.7975\,a - 2.3883\,b$.

384. A mixture of barium and strontium carbonates weighing 1.2601 g. contains 0.3192 g. of carbon dioxide. (*a*) What are

the weights of barium carbonate and strontium carbonate in the mixture? (*b*) What are the weights of barium and strontium in the mixture? *Ans.* (*a*) 0.7504 g. $BaCO_3$.
0.5097 g. $SrCO_3$.
(*b*) 0.5223 g. Ba.
0.3025 g. Sr.

385. Calculate the factors that applied to a problem such as 384 will give the weights of barium and strontium.

Ans. Ba = 2.7611 *a* − 9.2661 *b*.
Sr = 7.9025 *b* − 1.7617 *a*.

386. A sample of oleum weighing 3.1402 g. contains 2.7350 g. of sulphur trioxide. What per cent oleum is it?

Ans. 29.78% oleum.

387. What is the per cent total sulphur trioxide in 25% oleum?

Ans. 86.22%.

388. What is the per cent total sulphur trioxide in 15% oleum?

Ans. 84.38%.

389. If acetic anhydride $(CH_3CO)_2O$ will take up any water present to form acetic acid, what is the amount of uncombined acetic anhydride present in a sample of mixed acetic acid and acetic anhydride showing 87.72% anhydride present?

Ans. 18.13%.

CHAPTER IX

VOLUMETRIC ANALYSIS

"VOLUMETRIC analysis or quantitive chemical analysis by measure in the case of liquids and solids . . . depends upon the following conditions for its successful practice:

1. A solution of the reagent, the chemical value of which is accurately known, called the 'standard solution.'

2. A graduated vessel from which portions of it may be accurately delivered, called the 'burette.'

3. The decomposition [1] produced by the standard solution with any given substance must either in itself or by an indicator be such, that *its termination is unmistakable to the eye*, and thereby the quantity of the substance with which it has combined accurately calculated." [2]

Single-factor Solutions. — The standard solution may be made to any desired strength. If a solution is to be frequently used for the determination of a substance, for example iron, it is convenient to adjust its strength so that one cubic centimeter shows the presence of 0.01, 0.001 or 0.0001 g. of iron, in which case the determination of the weight of iron in grams present in the sample is obtained directly by the burette reading. If it is desired to make up a solution of silver nitrate, one cubic centimeter of which is to be equivalent to 0.001 g. of chlorine, and the weight of silver nitrate which must be

[1] "Reaction" might be a better word.

[2] Sutton, "Volumetric Analysis."

contained in a liter of the solution is to be calculated, the required weight can be found readily. The reaction is

$$M'Cl + AgNO_3 = M'NO_3 + AgCl.$$

The weight of chlorine which is to be indicated by one liter is

$$0.001 \times 1000. = 1.0000 \text{ g.}$$

The amount of silver nitrate necessary is

$$\frac{AgNO_3}{Cl} = \frac{169.89}{35.46} \times 1.0000 = 4.7910 \text{ g.}$$

It commonly occurs that a substance with which it is desired to make a standard solution cannot be weighed out in a state of purity; hence it is necessary to standardize the solution after it is made up. The methods of doing this are many: typical cases will be considered.

Methods of Standardization. — I. By weighing out the amount required and making up to the desired volume. This can be done only when the substance is in a state of purity and the weighing can be accurately performed and presents no great difficulties in manipulation. Among such substances may be mentioned sodium carbonate, arsenious oxide and sodium oxalate.

II. By causing a solution to react with a weighed amount of a chemically pure substance and measuring the volume of the solution necessary to do this. 0.21194 g. of anhydrous sodium carbonate require 40.00 cc. of a solution of hydrochloric acid to completely neutralize it. The strength of the hydrochloric acid per cubic centimeter is

$$\frac{2\,HCl}{Na_2CO_3} = \frac{2\,(36.47)}{106.00} \times \frac{0.21194}{40.00} = 0.003646 \text{ g. HCl per cc.}$$

III. By analyzing gravimetrically a measured portion of the solution. If 30.00 cc. of the same solution of

hydrochloric acid as above yield 0.4299 g. of silver chloride, the content of hydrochloric acid per cubic centimeter is

$$\frac{HCl}{AgCl} = \frac{36.47}{143.34} \times \frac{0.4299}{30.00} = 0.003646 \text{ g. HCl per cc.}$$

IV. By comparing a measured volume of the solution with a measured volume of another solution the strength of which is known and with which it reacts. If 45.00 cc. of the same hydrochloric acid solution react with 45.20 cc. of a solution of sodium hydroxide, each cubic centimeter of which contains 0.003982 g. of sodium hydroxide, the strength of the hydrochloric acid solution is

$$\frac{HCl}{NaOH} = \frac{36.47}{40.01} \times \frac{45.20 \times 0.003982}{45.00} = 0.003646 \text{ g. HCl per cc.}$$

Equivalent Values of Single-factor Solutions. — A solution may be made up to a strength to correspond to a simple factor, as, for instance, the solution of silver nitrate mentioned above, each cubic centimeter of which corresponds to a milligram of chlorine. When such a solution is to be used for another determination the value of the solution per cubic centimeter must be calculated for the new substance.

Potassium permanganate is a reagent used in a number of different volumetric determinations. Its value depends upon its oxidizing property. Iron is determined by it according to the equation

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O;$$

oxalic acid,

$$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O;$$

calcium when in the form of the oxalate,

$$2\,KMnO_4 + 5\,CaC_2O_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,CaSO_4 + 10\,CO_2 + 8\,H_2O;$$

manganese,

$$2\,KMnO_4 + 3\,MnSO_4 + 2\,H_2O = K_2SO_4 + 2\,H_2SO_4 + 5\,MnO_2.$$

There are many other similar reactions. If one cubic centimeter of the potassium permanganate solution represents 0.001 g. of iron, then as $2\,KMnO_4 \equiv 10\,Fe$, and $2\,KMnO_4 \equiv 5\,H_2C_2O_4$, it follows that $5\,H_2C_2O_4 \equiv 10\,Fe$: the amount of oxalic acid equivalent to one cubic centimeter of this permanganate solution is:

$$\frac{5\,H_2C_2O_4}{10\,Fe} = \frac{5\,(90.016)}{10\,(55.84)} \times 0.001 = 0.000806 \text{ g. } H_2C_2O_4 \text{ per cc.}$$

In like manner, $2\,KMnO_4 \equiv 10\,Fe$; $2\,KMnO_4 \equiv 5\,Ca$; then $5\,Ca \equiv 10\,Fe$, and the amount of calcium indicated by each cubic centimeter of the permanganate solution is

$$\frac{5\,Ca}{10\,Fe} = \frac{5\,(40.07)}{10\,(55.84)} \times 0.001 = 0.0003588 \text{ g. Ca per cc.}$$

Finally, as $2\,KMnO_4 \equiv 10\,Fe$ and $2\,KMnO_4 \equiv 3\,Mn$, it follows that $3\,Mn \equiv 10\,Fe$, and the value of the permanganate solution in terms of manganese is

$$\frac{3\,Mn}{10\,Fe} = \frac{3\,(54.93)}{10\,(55.84)} \times 0.001 = 0.0002951 \text{ g. Mn per cc.}$$

Factor Weights for Volumetric Solutions. — Factor weights[1] are as applicable to volumetric as to gravimetric analysis. Acetic acid is to be determined by titration with sodium hydroxide, one cubic centimeter of which contains 0.04006 g. What weight of acetic acid should be taken

[1] See p. 176.

such that the burette reading in cubic centimeters may show the percentage of acetic acid directly? One cubic centimeter of the sodium hydroxide solution is equivalent to

$$\frac{HC_2H_3O_2}{NaOH} = \frac{60.03}{40.06} \times 0.4006 = 0.06003 \text{ g. } HC_2H_3O_2 \text{ per cc.}$$

Supposing the acetic acid were 100% pure, the number of cubic centimeters required would be 100. This corresponds to $100 \times 0.06003 = 6.003$ g. of acetic acid. If this weight of acetic acid is weighed out and titrated with the sodium hydroxide under consideration, the burette reading in cubic centimeters will give the percentage of acetic acid present. Thus if 85.00 cc. of sodium hydroxide are required for neutralization, the acetic acid contains 85.00% $HC_2H_3O_2$ as is readily seen by the following:

$$\frac{85.00 \times 0.06003}{6.003} \times 100 = 85.00\% \, HC_2H_3O_2.$$

Instead of reading the percentage of acetic acid directly from the burette, it may be desirable to adjust the amount of acid taken, so that the burette reading multiplied by two gives the percentage of acetic acid.[1] If half of 6.003 g. (= 3.0015 g.), that is, fifty times the factor, is weighed out and titrated, the burette reading multiplied by two gives the percentage of acetic acid. If 42.50 cc. are required for titration, the percentage of acetic acid is $2 \times 42.50 = 85.00\%$, as is proved:

$$\frac{42.50 \times 0.06003}{3.0015} \times 100 = 85.00\% \, HC_2H_3O_2.$$

[1] This would be the case if a 50 cc. burette were used, as it would obviate the trouble of filling the burette a second time if the percentage exceeds 50%.

To put this in general terms; if the factor weight taken is m times the factor, the reading [1] must be multiplied by n, m and n being so chosen that their product equals 100. Thus, if the factor weight taken is five times the factor, the reading must be multiplied by twenty.

Normal Solutions. — "A normal solution of a reagent is one which contains, in a liter, that proportion of its molecular weight in grams which corresponds to one gram (gram atom) of available hydrogen or its equivalent." [2] Submultiples of the normal solution are used and are designated half or seminormal (N/2 or 0.5 N), fifth or quintinormal (N/5 or 0.2 N), tenth or decinormal (N/10 or 0.1 N), hundredth or centinormal (N/100 or 0.01 N), etc.

According to definition, the following weights of acids, bases or radicals contained in a liter are normal solutions:

Acetic acid (one available H ion) $= \frac{CH_3COOH}{1}$ [3] $= 60.032$ g.

[1] The reading may be in cubic centimeters, as in volumetric analysis, or in grams or some multiple of the gram, as in gravimetric analysis.

[2] Sutton, "Volumetric Analysis." The words "gram atom" in parenthesis have been inserted by the author, as in his opinion Sutton so intended. As the examples given by Sutton show, the normal solution contains 1.008 g. of available hydrogen and not 1.0000 g., as his definition would lead one to suppose. His definition would be exact if hydrogen were taken as unity in the determination of atomic weights. Such, however, is not the case, the basis being oxygen = 16 which makes hydrogen = 1.008.

[3] The expression is intended to represent a fraction, the numerical value of which is obtained by giving to the numerator a number equal to the molecular weight of the symbol. For a list of acids and bases and the values of normal solutions of the same, with the indicators to use in each case, see Chem. Ann., pp. 52–53. The solubilities of many substances are too small to permit of the preparation of a solution of normal strength. The values given indicate the weight of substance which would be present in a normal solution, solubility permitting. Such cases are illustrated by calcium

Ammonia	(one available NH_3 ion)	$= \frac{NH_3}{1}$	= 17.064 g.
Ammonium hydroxide	(one available OH ion)	$= \frac{NH_4OH}{1}$	= 35.08 g.
Hydrochloric acid	(one available H ion)	$= \frac{HCl}{1}$	= 36.47 g.
Nitric acid	(one available H ion)	$= \frac{HNO_3}{1}$	= 63.048 g.
Barium hydroxide	(two available OH ions)	$= \frac{Ba(OH)_2}{2}$	= 85.71 g.
Calcium hydroxide	(two available OH ions)	$= \frac{Ca(OH)_2}{2}$	= 37.06 g.
Sulphuric acid	(two available H ions)	$= \frac{H_2SO_4}{2}$	= 49.04 g.
Oxalic acid	(two available H ions)	$= \frac{C_2H_2O_4}{2}$	= 45.01 g.
Phosphoric acid [1]	(one available H ion)	$= \frac{H_3PO_4}{1}$	= 98.024 g.
Phosphoric acid [2]	(two available H ions)	$= \frac{H_3PO_4}{2}$	= 49.01 g.

Following is a list of a few oxidizing agents.[3] As one oxygen ion is equivalent to two hydrogen ions, the list will be evident.

and barium hydroxides, which on account of their limited solubility must be used in fractional normal solutions. Because of its low solubility, calcium hydroxide is not used in volumetric operations.

[1] As these solutions are used in neutralization, their value depends upon the acidity shown. When methyl orange is used as the indicator, the same shows color change when one hydrogen is replaced.

[2] When phenol-phthalein is used as the indicator, the color change takes place when two hydrogens are replaced.

[3] For a list of volumetric oxidizing and reducing agents with the values of a normal in each case, see Chem. Ann., pp. 54–55.

For a list of precipitation agents and data on the strengths of normal solutions of the same, see Chem. Ann., p. 56.

1 Iodine	(liberates or is ≡ 1 H ion)	$= \frac{I}{1}$	$= 127.92$ g.
1 Barium peroxide	(liberates 1 O ≡ 2 H ions)	$= \frac{BaO_2}{2}$	$= 84.7$ g.
1 Potassium dichromate	(liberates 3 O ≡ 6 H ions)	$= \frac{K_2Cr_2O_7}{6}$	$= 49.08$ g.
1 Potassium permanganate	(liberates $2\frac{1}{2}$ O ≡ 5 H ions)[1]	$= \frac{KMnO_4}{5}$	$= 31.63$ g.
1 Arsenious oxide	(takes up 2 O ≡ 4 H ions)	$= \frac{As_2O_3}{4}$	$= 49.5$ g.

In order to determine the amount of substance which must be present to form a solution of a required normality, the particular reaction in which the solution takes part must be known. Thus, in an acid solution, two molecules of potassium permanganate liberate five atoms of oxygen. Permanganic acid is $HMnO_4$; the anhydride would be

$$2\,HMnO_4 = Mn_2O_7 + H_2O.$$

In acid solution, the decomposition may be abbreviated to

$$Mn_2O_7 = 2\,MnO + 5\,O.$$

Then as 5 O ≡ 10 H, the weight of salt requisite in a liter of a normal solution when used in an acid condition is

$$\frac{2\,KMnO_4}{10} = \frac{KMnO_4}{5} = \frac{158.15}{5} = 31.63\text{ g. } KMnO_4.$$

In an alkaline solution the essential features may be represented by

$$2\,Mn_2O_7 = 2\,MnO_2 + 3\,O.$$

Hence, when potassium permanganate is to be used in an alkaline solution, the weight necessary for a liter of a normal solution is

$$\frac{2\,KMnO_4}{6} = \frac{KMnO_4}{3} = \frac{158.15}{3} = 52.7166\text{ g. } KMnO_4.^2$$

[1] That is, two molecules of $KMnO_4$ yield five oxygens in an acid solution.

[2] Potassium permanganate is rarely titrated in an alkaline or neutral solution. An example is the titration of manganese. See

The calculation of the normal quantity of a salt is not always such a simple matter. The normal quantity of hydrochloric acid being 36.47, in the reaction

$$NH_4OH + HCl = NH_4Cl + H_2O,$$

the weight of ammonium chloride equivalent to this weight of hydrochloric acid, and, consequently, the normal quantity of ammonium chloride in this reaction, is

$$\frac{NH_4Cl}{HCl} = \frac{53.502}{36.47} \times 36.47 = 53.502 \text{ g.}$$

In like manner the amount of ammonium sulphate is obtained from the equation

$$2\,NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2\,H_2O;$$

consequently, the normal weight (the weight in grams per liter, the normal weight of sulphuric acid being 49.04 g.) is

$$\frac{(NH_4)_2SO_4}{H_2SO_4} = \frac{132.15}{98.09} \times 49.04 = 66.068 \text{ g.}$$

Simplification of Calculations by the Use of Normal Solutions. — Knowing the reaction, when normal quantities are used, the weights of the substances involved may be found by inspection. Defining oxidation as the process of adding oxygen to, or the removal of hydrogen from, or raising the valence of, the substance oxidized, and reduction as the reverse, the normal weights of compounds that are neither acids nor bases, but will react with oxidizing or reducing compounds, are readily determined. The oxidation of iron raises its valence from two to three, a gain of one in valence, which is equivalent to

reaction, Prob. 391. For other examples, see phosphoric acid with different indicators, p. 208. When a normal solution of potassium permanganate is spoken of, the solution equivalent to five oxygens is understood unless specifically qualified.

one hydrogen. Hence, the normal amount of iron, *i.e.*, the amount of iron shown by a liter of any normal oxidizing or reducing reagent used for its determination, is $\frac{55.84}{1} = 55.84$ g. Antimonious salts when acted upon by certain oxidizing agents are converted into antimonic salts, *i.e.*, antimony is changed from the trivalent to the pentavalent condition, a gain in valence of two; hence, the weight of antimony shown by a normal weight of oxidizing or reducing substances is

$$\frac{Sb}{2} = \frac{120.2}{2} = 60.10 \text{ g.}$$

Normal solutions are of such strength that equal volumes are exactly equivalent; thus, one normal cubic centimeter of an acid exactly neutralizes one normal cubic centimeter of a base, producing a neutral solution.[1] Knowing the normality of a solution, its value in terms of any constituent with which it reacts can be calculated easily, and can often be done by inspection. If 30.00 cc. of an N/10 solution of sodium hydroxide are used to determine hydrochloric acid in a 2.0000 g. sample, the amount of hydrochloric acid present is (1.00 cc. N/10 HCl $= \frac{HCl}{1000 \times 10} = 0.003647$ g. HCl)

$$30.00 \times 0.003647 = 0.10941 \text{ g.};$$

[1] There is another system of concentrations. This is the *Molar* system and is used chiefly in physical chemistry. A molar solution contains one gram molecule of solute per liter of solution. Under this definition a molar solution of hydrochloric acid contains 36.468 g. HCl per liter as does also a normal solution. A molar solution of sulphuric acid contains 98.086 g. H_2SO_4 per liter, while a normal solution contains 49.043 g. So it is seen that a molar and a normal solution may or may not be equivalent.

and as 2.0000 g. of sample were taken, the percentage of hydrochloric acid is

$$\frac{30.00 \times 0.003647}{2.0000} \times 100 = 5.47\% \text{ HCl.}$$

If the 30.00 cc. had been used in the determination of sulphuric acid, the same amount being taken (1.00 cc. N/10 $H_2SO_4 = \frac{\frac{1}{2} H_2SO_4}{1000 \times 10} = 0.004904$ g. H_2SO_4), the result would have been

$$\frac{30.00 \times 0.004904}{2.0000} \times 100 = 7.36\% \ H_2SO_4.$$

Again, potassium permanganate is used to determine iron, calcium in the form of oxalate, and also nitrous acid. 45.00 cc. of a 0.1 N[1] solution of potassium permanganate are required to bring about the reactions. The amounts present can be readily determined without recourse to stoichiometric ratios in the form of a reaction. Iron is oxidized by permanganate, the valence being increased by one. If all the iron were present in the ferrous condition, then as the amount of iron shown by one cubic centimeter of 0.1 N potassium permanganate is

$$\frac{\text{Fe}}{1 \times 1000 \times 10} = 0.005584 \text{ g.},$$

the total amount of iron is

$$45.00 \times 0.005584 = 0.2513 \text{ g. Fe.}$$

The calcium is separated as the oxalate which on treatment with sulphuric acid liberates one molecule of oxalic acid for each atom of calcium present. The oxalic acid is oxidized by the permanganate, one atom of oxygen being taken up for each molecule of oxalic acid present. Then, as one oxygen is equivalent to two hydrogens, the

[1] The normality of a solution may as well be expressed as a decimal as a fraction; in fact, the decimal system is to be preferred.

amount of calcium equivalent to a cubic centimeter of a tenth normal oxidizing solution is

$$\frac{\text{Ca}}{2 \times 1000 \times 10} = 0.0020035 \text{ g.}$$

The amount of calcium present is

$$45.00 \times 0.0020035 = 0.090158 \text{ g. Ca.}$$

Potassium permanganate oxidizes nitrous acid to nitric acid, a gain of one atom of oxygen which is equivalent to two hydrogens. The amount of nitrous acid equivalent to a cubic centimeter of a decinormal solution is

$$\frac{\text{HNO}_2}{2 \times 1000 \times 10} = 0.002351 \text{ g.}$$

The amount of nitrous acid present is

$$45.00 \times 0.002351 = 0.1058 \text{ g. HNO}_2.$$

Calculation of Normality. Factor to a Given Normality. — Thus far solutions have been considered as being adjusted to the normality indicated. This is a matter of considerable difficulty and it is a general practice to calculate the strength of solutions by methods already given, not attempting to have the normality more than approximate, the exact strength, however, always being known. A solution shows on standardization 0.02458 g. of sulphuric acid per cubic centimeter. A normal solution of this acid contains 0.049045 g. per cubic centimeter; then the normality of this solution is

$$\frac{0.02458}{0.049045} = 0.5012 \text{ N.}$$

This shows the solution to be very nearly half normal, being a little strong. The factor to exactly half normal is

$$\frac{0.5012}{0.5000} = 1.002.$$

$$\frac{11.00}{50.00} \times 0.5200 = 0.1144\,\text{N},$$

or substituting in the formula gives

$$50.00 \times \text{N}' = 11.00 \times 0.5200,$$

$$\text{N}' = \frac{11.00}{50.00} \times 0.5200 = 0.1144\,\text{N}.$$

Again, how many cubic centimeters of a solution whose factor to N/10 is 0.9924 are equivalent to 18.00 cc. of a solution whose factor to N/2 is 1.005? The number of cubic centimeters of N/10 solution equivalent to a solution whose factor to N/10 is 1.005, is $18.00 \times 1.005 = 18.09$ cc. This number of cubic centimeters of N/10 solution is equivalent to $18.09 \times 5 = 90.45$ cc. of N/2 solution. Then the number of cubic centimeters of a solution whose factor to N/2 is 0.9924 equivalent to 90.45 cc. N/2 solution is

$$\frac{1.0000}{0.9945} \times 90.45 = 91.14\,\text{cc}.$$

Solving in another manner: The normality of the first solution, expressed decimally, is $0.1 \times 0.9924 = 0.09924$ N. The normality of the second solution, similarly expressed, is $0.5 \times 1.005 = 0.5025$ N. Then

$$\frac{0.5025}{0.09924} \times 18.00 = 91.14\,\text{cc}.$$

Volumetric Determinations Using Two Solutions. Back Titrations. — Many volumetric analyses are carried out by the use of two solutions. These methods generally consist in adding an excess of the active reagent and determining this excess by means of a suitable second solution with which the first reacts. It is necessary to know the relative strengths of the two solutions employed so that the amount of the solution used in pro-

ducing the desired reaction may be ascertained. When the two solutions are exactly equivalent, cubic centimeter to cubic centimeter, subtraction of the volumes used gives the amount of the first solution necessary to bring about the desired reaction.

A sample of calcium carbonate is to be analyzed, phenol-phthalein being used as the indicator, which is affected by the carbonic acid liberated when the calcium carbonate is treated with an acid; hence, the end point in this titration would occur too soon, were it attempted to titrate directly to a finish with sulphuric acid alone. A solution of sulphuric acid of exactly 0.1 N strength and a solution of exactly 0.1 N sodium hydroxide are employed. 0.2000 g. of the sample are weighed out, water added, and treated with 45.00 cc. of the 0.1 N sulphuric acid and the solution boiled to expel the carbon dioxide. The solution is now acid with sulphuric acid, 6.45 cc. of 0.1 N sodium hydroxide being required to produce neutrality. The amount of sulphuric acid used in decomposing the calcium carbonate is evidently 45.00 − 6.45 = 38.55 cc. of 0.1 N solution. Assuming that there are no other carbonates present, the equivalent of one cubic centimeter of 0.1 N solution of sulphuric acid in terms of calcium carbonate being $\frac{CaCO_3}{2 \times 1000 \times 10} = 0.0050035$ g., the percentage of calcium carbonate in the sample taken is

$$\frac{38.55 \times 0.0050035}{0.2000} \times 100 = 96.44\% \, CaCO_3.$$

Calcium acetate, $Ca(C_2H_3O_2)_2 \cdot H_2O$, is to be examined for the percentage of the same present in a sample weighing 3.7246 g. The calcium acetate is digested with an excess of syrupy phosphoric acid, the acetic acid liberated being distilled into 50.00 cc. of 1.005 N sodium hydroxide

solution. The excess of sodium hydroxide required 55.25 cc. of 0.2012 N sulphuric acid for neutralization.

$50.00 \times 1.005 = 50.25$ cc. of 1 N NaOH solution taken,

$\frac{0.2012}{0.2000} \times 55.25 = 55.58$ cc. of 0.2 N H_2SO_4 for back titration,

55.58 cc. of 0.2 N $H_2SO_4 \equiv 0.2 \times 55.58 = 11.12$ cc. of 1 N H_2SO_4,

$50.25 - 11.12 = 39.13$ cc. of 1 N NaOH consumed.

Then, as $Ca(C_2H_3O_2)_2 \cdot H_2O \equiv 2\,HC_2H_3O_2 \equiv 2$ NaOH, the amount of calcium acetate indicated by one cubic centimeter of normal sodium hydroxide being

$$\frac{Ca(C_2H_3O_2)_2 \cdot H_2O}{2 \times 1000} = 0.088065 \text{ g.},$$

the per cent of calcium acetate is

$$\frac{39.13 \times 0.088065}{3.7246} \times 100 = 92.52\%\ Ca(C_2H_3O_2)_2 \cdot H_2O.$$

Titration of "Mixed Acid." — A mixture of substances may be analyzed volumetrically. A sample of "mixed acid" contains sulphuric acid, nitric acid and lower oxides of nitrogen, chiefly N_2O_3, which result from mixing the two acids.

A sample is taken, treated with water and evaporated on the steam bath, the operation being repeated twice, which treatment leaves only sulphuric acid which is titrated with standard alkali solution. A second sample is titrated with standard alkali for total acidity and a third sample with potassium permanganate for nitrous anhydride.

Data for determination of mixed acid:

For total acid:

Weight of sample taken = 4.6514 g.
NaOH to neutralize = 74.10 cc.
1.00 cc. NaOH sol. ≡ 0.052109 g. H_2SO_4.

Per cent total acid as H_2SO_4 is

$$\frac{74.10 \times 0.052109}{4.6514} \times 100 = 83.01\%.$$

For sulphuric acid ($HNO_3 + HNO_2$ being driven off by evaporation):

Weight of acid taken = 8.8872 g.
NaOH to neutralize = 72.20 cc.
1.00 cc. NaOH sol. ≡ 0.052109 g. H_2SO_4.

Per cent sulphuric acid is

$$\frac{72.20 \times 0.052109}{8.8872} \times 100 = 42.33\%.$$

For nitrous anhydride:

Weight of sample taken = 17.000 g.
0.1 N $KMnO_4$ to oxidize N_2O_3 to N_2O_5 = 8.60 cc.
1.00 cc. of 0.1 N $KMnO_4$ ≡ 0.001900 g. N_2O_3.

Per cent nitrous anhydride is

$$\frac{8.60 \times 0.0019}{17} = 0.096\% = 0.10\%.$$

To calculate the composition of the mixed acid:

$83.01 - 42.33 = 40.68\%$ $HNO_3 + HNO_2$ as H_2SO_4.

The amount of acidity as nitric acid is

$$\frac{2\,HNO_3}{H_2SO_4} = \frac{2\,(63.02)}{98.09} \times 40.68 = 52.27\%\ HNO_3 + HNO_2 \text{ as } HNO_3.$$

The equivalent of N_2O_3 in HNO_3 is

$$\frac{2\,HNO_3}{N_2O_3} = \frac{2\,(63.02)}{76.02} \times 0.096 = 0.16\%.$$

The amount of nitric acid present is

$$52.27 - 0.16 = 52.11\%\ HNO_3.$$

From these figures the analysis of the mixed acid is

	Per cent
Sulphuric acid	42.33
Nitric acid	52.11
Nitrogen trioxide	0.10
Water (by difference)	5.46
	100.00

Volumetric Analysis Using Two Indicators. — Mixtures may also be analyzed by taking advantage of the conduct of different salts toward indicators.[1] For example, phenol-phthalein reacts alkaline to sodium carbonate, neutral to bicarbonate, and acid to carbonic acid.[2] If a mixture of sodium hydroxide and sodium carbonate is treated with a known amount of hydrochloric acid till the solution reacts just acid to phenol-phthalein, the following will be the reaction:

$$(1)\quad x\,NaOH + y\,Na_2CO_3 + (x+y)\,HCl = y\,NaHCO_3 + x\,H_2O + (x+y)\,NaCl.$$

If the titration is continued, boiling out the carbonic acid, the solution will react neutral to methyl orange when the bicarbonate is decomposed:

$$(2)\quad y\,NaHCO_3 + y\,HCl = y\,NaCl + y\,H_2O + y\,CO_2.$$

[1] See Chem. Ann., p. 51.

[2] Phenol-phthalein as an indicator is used to show the presence of minute amounts of strong bases or weak acids. Methyl orange indicates the presence of minute amounts of weak bases and strong acids. For strong acids and strong bases either will serve. Methyl red is an indicator which acts similarly to methyl orange and possesses advantages over the latter, being nearly colorless in a basic and a strong red in an acid solution.

Then, if p represents the total hydrochloric acid used, and q the hydrochloric acid used to convert the sodium hydroxide and the sodium carbonate into sodium chloride and sodium bicarbonate,

$$\begin{aligned} x + 2y &= p \\ x + \ \ y &= q \\ \hline y &= p - q \\ x &= 2q - p. \end{aligned}$$

To illustrate: one-half gram of a sample composed of sodium hydroxide and sodium carbonate requires 62.50 cc. N/10 hydrochloric acid to neutral reaction with phenolphthalein. The titration is continued; 100.00 cc. of the same acid are required for complete neutrality (methyl orange). The last addition of hydrochloric acid is a measure of the sodium carbonate present, for all the sodium hydroxide was neutralized with the first addition of acid.

$$100.00 - 62.50 = 37.50 \text{ cc. of N/10 HCl for } NaHCO_3 \rightarrow NaCl, H_2O, CO_2.$$

The amount of bicarbonate is equivalent to the amount of sodium carbonate originally present. 1 cc. of N/10 HCl = $\frac{Na_2CO_3}{1000 \times 10} = 0.010600$ g. of sodium carbonate, as only one acid hydrogen is present in the acid carbonate. Then

$$\frac{37.50 \times 0.010600}{0.5000} \times 100 = 79.50\% \ Na_2CO_3.$$

The same amount of hydrochloric acid is used to convert the bicarbonate into sodium chloride, carbon dioxide and water as was required to convert the sodium carbonate into bicarbonate. Therefore, 62.50 − 37.50 = 25.00 cc. of N/10 HCl, used in reacting with the sodium hydroxide.

1 cc. of N/10 HCl $\equiv \frac{\text{NaOH}}{1000 \times 10} = 0.004001$ g. sodium hydroxide. Then

$$\frac{25.00 \times 0.004001}{0.5000} \times 100 = 20.01\% \text{ NaOH.}$$

Algebraically, according to the equations given, letting

x = cc. of N/10 acid combining with NaOH,

y = cc. of N/10 acid required to change Na_2CO_3 to $NaHCO_3$ and $NaHCO_3$ to NaCl, CO_2 and H_2O.

Then

$x = 125.00 - 100.00 = 25.00$ cc. N/10 HCl,

$y = 100.00 - 62.50 = 37.50$ cc. N/10 HCl.

The calculation is completed as given above.

Volumetric Titration of Oleum. — When an oleum contains free sulphurous anhydride, an interesting and important case of indirect volumetric analysis results. Such an oleum contains sulphuric acid, sulphurous anhydride (SO_2) and sulphuric anhydride (SO_3).[1] A weighed sample is dissolved in water and titrated with a standard alkali solution, when all the constituents are acted upon. Thus, for sulphuric acid:

$$H_2SO_4 + 2\,NaOH = Na_2SO_4 + 2\,H_2O.$$

The sulphuric anhydride dissolves in water to form sulphuric acid and is titrated:

$$SO_3 + H_2O = H_2SO_4,$$
$$H_2SO_4 + 2\,NaOH = Na_2SO_4 + 2\,H_2O.$$

Likewise, the sulphurous anhydride dissolves:

$$SO_2 + H_2O = H_2SO_3.$$

[1] There may be other impurities, such as solid particles, etc., but for these calculations, only the three constituents enumerated will be considered as being present. The method is easily extended to cover impurities.

When phenol-phthalein is used as an indicator, the reaction with the alkali is

$$H_2SO_3 + 2\,NaOH = Na_2SO_3 + 2\,H_2O,$$

while with sodium hydroxide, using methyl orange as an indicator, it is

$$H_2SO_3 + NaOH = NaHSO_3 + H_2O.$$

The sulphurous anhydride is estimated in a separate sample by dissolving the oleum in water and titrating against an iodine solution:

$$H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2\,HI.$$

An example of an oleum analysis follows: 5.0000 g. of an oleum are dissolved in water and the volume made up to 500 cc. Of this solution, 100 cc. (= 1.0000 g. of sample) are taken and titrated with N/10 iodine solution, 7.80 cc. being required. A similar portion is taken and titrated with N/5 sodium hydroxide, using phenol-phthalein as an indicator, 122.81 cc. being required. To calculate the composition of the oleum:

$$\frac{7.80 \times 0.0032035}{1.0000} \times 100 = 2.50\%\ SO_2,$$

122.81 N/5 sol. = $2 \times 122.81 = 245.62$ cc. N/10 sol.,
$245.62 - 7.80 = 237.82$ cc. N/10 NaOH

required for the titration of the sulphuric acid and sulphur trioxide.[1]

[1] The 7.80 cc. are subtracted, this being the number of cubic centimeters of N/10 solution of sodium hydroxide used in neutralizing the sulphurous acid. If methyl orange had been used, 253.42 cc. of N/10 sodium hydroxide would have been necessary for the total acidity titration, but 15.6 cc. of N/10 solution would have to be deducted from the 253.42 cc. N/10 sodium hydroxide required for the total acidity, leaving 237.82 cc. necessary for the sulphuric acid and the sulphuric anhydride, as before.

$$\frac{237.82 \times 0.0040035}{1.0000} \times 100 = 95.21\% \text{ total } SO_3,$$

$$95.21 + 2.50 = 97.71\% \, SO_3 + SO_2,$$

$$100.00 - 97.71 = 2.29\% \, H_2O.$$

Calculating this percentage of water into equivalent sulphuric acid:

$$\frac{98.09}{18.016} \times 2.29 = 12.47\% \, H_2SO_4.$$

Then

$$100.00 - (12.47 + 2.50) = 85.03\% \text{ free } SO_3.$$

To summarize, the oleum is composed of

	Per cent
H_2SO_4	12.47
SO_3	85.03
SO_2	2.50

To calculate algebraically, let

x = per cent of H_2SO_4,

y = per cent of SO_3,

z = per cent of SO_2,

A = percentage total acidity as H_2SO_4, *not* including that due to SO_2,

$$f = \text{factor} \frac{H_2SO_4}{SO_3} = \frac{98.09}{80.07} = 1.22505.$$

Then

$$\begin{aligned} x + y + z &= 100 \\ x + y &= 100 - z \\ x &= 100 - (z + y). \end{aligned}$$

From the conditions of the problem:

$$\begin{aligned} x + y &= 100 - z \\ x + fy &= A \end{aligned}$$

$$y = \frac{A + z - 100}{f - 1} = \frac{A + z - 100}{0.22505}$$

$$= 4.4436 \, (A + z - 100).$$

Solving the given problem by this method:

$$z = 2.50 \text{ (as before)},$$

$$A = \frac{237.82 \times 0.0049045}{1.0000} \times 100 = 116.64\%,$$

$$y = 4.4436\,(116.64 + 2.50 - 100) = 4.4436 \times 19.14 = 85.05\%,$$

$$x = 100 - (2.50 + 85.05) = 12.45\%,$$

which results are the same as were obtained by the method given before.[1]

Adjustment of the Strength of Solutions. — Having a solution containing 47% HNO_3, and a weaker solution of 23% HNO_3, let it be required to prepare, by mixing these two solutions, 200 kg. of a solution which will contain 39% HNO_3. To find the weights of the two solutions, which, when mixed, will give the desired quantity of acid of the specified strength, let y = the weight of the weaker acid (23% HNO_3) to be taken; then $200 - y$ = the weight of the stronger acid (47% HNO_3) to be taken. Algebraically:

$$0.23\,y + 0.47\,(200 - y) = 0.39\,(200),$$

$$y = 66.67 \text{ kg. } 23\% \text{ } HNO_3,$$

$$200 - 66.67 = 133.33 \text{ kg. } 47\% \text{ } HNO_3.$$

Using this method, a general formula may be obtained. Let

A = strength of stronger solution,
B = strength of weaker solution,
D = strength of desired solution,
x = amount of stronger solution to be taken,
y = amount of weaker solution to be taken,
z = amount of solution desired.

[1] An oleum analyzed by these methods must necessarily foot up to 100% as the free SO_3 is calculated by difference.

Then

$$By + A(z - y) = Dz,$$
$$By + Az - Ay = Dz,$$
$$y(B - A) = z(D - A),$$
$$y = \frac{D - A}{B - A}z = \frac{A - D}{A - B}z,$$
$$x + y = z,$$
$$x = z - y.$$

Again, suppose the problem is to alter the strength of a definite quantity of acid. Given, an acid of 47% HNO_3, let it be required to dilute 200 kg. of this acid to 39% HNO_3, using 23% HNO_3. What weight of 23% HNO_3 must be added to 200 kg. to make the mixture 39% HNO_3? Using the same symbols as before:

$$0.47(200) + 0.23y = 0.39(200 + y),$$
$$y = 100 \text{ kg. } 23\% \text{ } HNO_3.$$

In general terms

$$Ax + By = D(x + y),$$
$$y(B - D) = x(D - A),$$
$$y = \frac{D - A}{B - D}x = \frac{A - D}{D - B}x.$$

The following formulas, derived by the processes given above, are very convenient for adjusting the strength of solutions. In these, let

A = actual concentration of the solution that is to be corrected,
D = desired concentration,
B = concentration of diluting solution,
C = concentration of strengthening solution,
x = amount of stronger solution to be added, taken or prepared,

y = amount of weaker solution or water to be added or taken,

z = amount of solution desired or given.

Formulas (*a*) are to be used when a definite amount of the solution is to be *prepared*. Formulas (*b*) are to be used when a definite amount of solution is to be *corrected*, *i.e.*, strengthened or weakened.

I. *To dilute a solution with water:*[1]

(*a*) $\frac{D}{A}z = x, \qquad y = z - x.$

(*b*) $\frac{A - D}{D}x = y.$

II. *To dilute a strong liquid with a weaker liquid:*

(*a*) $\frac{A - D}{A - B}z = y, \quad x = z - y.$

(*b*) $\frac{A - D}{D - B}x = y.$

[1] The Giles flask is a convenient instrument for preparing a solution of definite strength. The neck of the flask is blown out into a bulb. The lower mark below the bulb is the mark for the indicated capacity of the flask, while above the bulb is another mark indicating a capacity between it and the lower mark of one-tenth the indicated capacity of the flask. To make up a standard solution, 11/10 plus a small amount required for the volume *indicated* are weighed out and introduced into the flask. Water is filled to the upper mark and a sample pipetted out of the flask, such sample not exceeding the capacity of the bulb between the upper and lower marks. This is titrated and the solution drawn off to the lower mark (the mark of the indicated capacity). As the solution was purposely made a trifle strong, water must be added to adjust to the strength desired. The amount of liquid being known, the amount of water to add is calculated by (*b*).

III. *To strengthen a weak solution with a stronger solution:*

(*a*) $\frac{D-A}{C-A}z = x, \quad y = z - x.$

(*b*) $\frac{D-A}{C-D}y = x.$[1]

PROBLEMS

390. How many grams per liter must a solution of potassium dichromate contain so that each cubic centimeter shall show 0.005000 g. of iron according to the reaction:

$$6\,FeCl_2 + K_2Cr_2O_7 + 14\,HCl = 6\,FeCl_3 + 2\,KCl + 2\,CrCl_3 + 7\,H_2O?$$

Ans. 4.3905 g.

391. How much potassium permanganate per liter must a solution contain to be of such strength that each cubic centimeter is equivalent to 0.001000 g. of manganese? The reaction is

$$2\,KMnO_4 + 3\,MnSO_4 + 7\,H_2O = 2\,KHSO_4 + H_2SO_4 + 5\,H_2MnO_3.$$

Ans. 1.9180 g.

392. It is desired to make up a solution of potassium dichromate of such strength that one cubic centimeter will indicate 0.001000 g. of iron. (*a*) How many grams of the potassium dichromate must be contained in a liter? (*b*) How many

[1] These formulas are universally accurate when the *weights* of solution are considered. If the solutions are dilute, the specific gravities may be considered, with but little error, as being the same as water. In this case, the formulas may be used for volumes. When this assumption is not permissible, the weights may be calculated, and knowing the specific gravities of the components, the volumes requisite calculated from the formula, volume $= \frac{\text{mass}}{\text{sp. gr.}}$. On mixing such concentrated solutions, to use these formulas it must be assumed that the volumes are additive, *i.e.*, no change of volume takes place.

grams of potassium dichromate, that each cubic centimeter shall show 0.001000 g. Fe_2O_3? The reaction is

$$6\,FeCl_2 + K_2Cr_2O_7 + 14\,HCl = 6\,FeCl_3 + 2\,KCl + 2\,CrCl_3 + 7\,H_2O.$$

Ans. (*a*) 0.8781 g.
(*b*) 0.6141 g.

393. How many grams of potassium permanganate per liter must a solution contain, each cubic centimeter of which is to be equivalent to 0.001000 g. of iron according to the equation:

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O.$$

Ans. 0.5660 g.

394. Calcium is separated as the oxalate which is treated with sulphuric acid and the oxalic acid liberated is titrated with potassium permanganate. The reactions are

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2\,NH_4Cl,$$
$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4,$$
$$5\,H_2C_2O_4 + 2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O.$$

How many grams per liter of potassium permanganate are required that one cubic centimeter shall show (*a*) 0.001000 g. of calcium? (*b*) 0.001000 g. of calcium oxide? (*c*) 0.01000 g. of $CaSO_4 \cdot 2\,H_2O$? *Ans.* (*a*) 1.5776 g.
(*b*) 1.1300 g.
(*c*) 3.6715 g.

395. What weight of silver nitrate must be taken, dissolved and made up to a liter that each cubic centimeter shall be equivalent to a milligram of sodium chloride according to the reaction:

$$NaCl + AgNO_3 = NaNO_3 + AgCl.$$

Ans. 2.9060 g.

396. Arsenious oxide acts as a reducing agent:

$$As_2O_3 + 2\,O = As_2O_5.$$

How much arsenious oxide must be weighed out, dissolved and made up to a liter that each cubic centimeter shall take up 0.001000 g. of oxygen or its equivalent? *Ans.* 6.1850 g.

397. A solution contains 67.0000 g. of sodium oxalate in a liter. If it reacts as follows:

$$Na_2C_2O_4 + H_2SO_4 = Na_2SO_4 + H_2C_2O_4,$$
$$H_2C_2O_4 = H_2O + CO_2 + CO,$$
$$CO + O = CO_2,$$

how much oxygen is taken up per cubic centimeter?

Ans. 0.0080 g.

398. A solution contains 10.0000 g. of silver nitrate made up to a liter. What is the content of silver per cubic centimeter?

Ans. 0.006350 g.

399. 30.20 cc. of a solution of sulphuric acid neutralizes 0.1708 g. of pure anhydrous sodium carbonate. What is the amount of sulphuric acid in the solution per cubic centimeter?

Ans. 0.0052335 g.

400. 0.5000 g. of pure arsenious oxide are dissolved: 100.00 cc. of a solution of iodine are necessary to oxidize the arsenious oxide:

$$As_2O_3 + 2\,I_2 + 2\,H_2O = As_2O_5 + 4\,HI.$$

What is the strength of the iodine solution per cubic centimeter?

Ans. 0.012826 g.

401. 0.1062 g. of iron 99.8% pure are converted into ferrous sulphate and require 19.00 cc. of potassium permanganate to oxidize to ferric sulphate:

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O.$$

What is the content of potassium permanganate per cubic centimeter in this solution? *Ans.* 0.003157 g.

402. 0.2680 g. of pure sodium oxalate are weighed out and dissolved in water. 40.00 cc. of potassium permanganate solution are required to react with this amount of sodium oxalate:

$$2\,KMnO_4 + 5\,Na_2C_2O_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Na_2SO_4 + 10\,CO_2 + 8\,H_2O.$$

What is the content of potassium permanganate per cubic centimeter? *Ans.* 0.0031606 g.

403. 50.00 cc. of a solution of hydrochloric acid are treated with silver nitrate, yielding 0.7167 g. of silver chloride. What is the weight of hydrochloric acid per cubic centimeter?
Ans. 0.003647 g.

404. A solution of sulphuric acid is standardized by precipitation as barium sulphate. 30.00 cc. gave 0.3500 g. of barium sulphate. What is the strength of the sulphuric acid solution per cubic centimeter? *Ans.* 0.004903 g.

405. 45.00 cc. of a solution of barium hydrate when precipitated with sulphuric acid yield 0.6842 g. of barium sulphate. (*a*) What is the content of barium hydroxide per cubic centimeter? (*b*) To how many grams of hydrochloric acid per cubic centimeter is this solution equivalent? *Ans.* (*a*) 0.011164 g.
(*b*) 0.004751 g.

406. 25.00 cc. of a solution of sulphuric acid yield 0.5852 g. of barium sulphate. What is the content of sulphuric acid per cubic centimeter of this solution? *Ans.* 0.0098355 g.

407. What is the strength of a solution of barium hydroxide if 30.00 cc. require for neutralization 59.80 cc. of a solution of sulphuric acid known to contain 0.004900 g. per cubic centimeter? *Ans.* 0.01707 g.

408. It is found that 32.50 cc. of a solution of sodium hydroxide exactly neutralize 30.00 cc. of a solution of sulphuric acid known to contain 0.04902 g. per cubic centimeter. What is the strength of the sodium hydroxide solution per cubic centimeter?
Ans. 0.03691 g.

409. A solution of sodium hydroxide is equivalent to 0.004875 g. of sulphuric acid per cubic centimeter. (*a*) What is its equivalent in nitric acid per cubic centimeter? (*b*) Hydrochloric acid? *Ans.* (*a*) 0.006264 g.
(*b*) 0.003625 g.

410. One cubic centimeter of a solution of potassium permanganate is equivalent to 0.005000 g. of iron. What is its equivalent of $KH_3(C_2O_4)_2 \cdot 2\,H_2O$, the reaction being

$$10\,KH_3(C_2O_4)_2 + 8\,KMnO_4 + 17\,H_2SO_4 = 9\,K_2SO_4 + 8\,MnSO_4 + 40\,CO_2 + 32\,H_2O?$$

Ans. 0.005689 g.

411. One cubic centimeter of a solution of potassium permanganate is equivalent to 0.005585 g. of iron. To how much potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3\,H_2O$, per cubic centimeter, is this solution equivalent, the reaction being

$$10\,K_4Fe(CN)_6 + 2\,KMnO_4 + 8\,H_2SO_4 = 10\,K_3Fe(CN)_6 + 6\,K_2SO_4 + 2\,MnSO_4 + 8\,H_2O?$$

Ans. 0.042236 g.

412. A solution of potassium dichromate is equivalent to 0.005000 g. of iron per cubic centimeter:

$$K_2Cr_2O_7 + 6\,FeCl_2 + 14\,HCl = 2\,KC + 2\,CrCl_3 + 6\,FeCl_3 + 7\,H_2O;$$

if the solution is used to determine antimony:

$$K_2Cr_2O_7 + 3\,SbCl_3 + 14\,HCl = 3\,SbCl_5 + 2\,CrCl_3 + 2\,KCl + 7\,H_2O,$$

what is the equivalent of antimony per cubic centimeter of this solution? *Ans.* 0.005381 g.

413. A permanganate solution is equivalent to 0.005000 g. of iron per cubic centimeter according to the reaction:

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O;$$

if it is used to determine nitrous acid according to the equation:

$$2\,KMnO_4 + 5\,HNO_2 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,HNO_3 + 3\,H_2O:$$

(*a*) What is the value of the permanganate solution per cubic centimeter in terms of nitrous acid? (*b*) In terms of nitrous anhydride, (N_2O_3)? *Ans.* (*a*) 0.002105 g.
(*b*) 0.001702 g.

414. How many grams per cubic centimeter are contained in an N/2 solution of (*a*) potassium carbonate and (*b*) potassium

bicarbonate, when the solutions are used to neutralize acids? (The reaction results in decomposition to carbon dioxide.)

Ans. (*a*) 0.03455 g.
(*b*) 0.05054 g.

415. How many grams per cubic centimeter are contained in a 0.1 N solution of acetic acid? *Ans.* 0.006003 g.

416. What is the normal quantity of (*a*) barium sulphate? (*b*) Barium chloride? (*c*) Silver chloride?

Ans. (*a*) 116.72 g.
(*b*) 104.15 g.
(*c*) 143.34 g.

417. How many grams per cubic centimeter in an N/10 solution of (*a*) ferrous sulphate ($FeSO_4 \cdot 7\,H_2O$), and (*b*) ferrous ammonium sulphate ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$), when used with an oxidizing agent? *Ans.* (*a*) 0.027802 g.
(*b*) 0.039216 g.

418. Potassium tetroxalate, $KH_3(C_2O_4)_2 \cdot 2\,H_2O$, as an acid reacts:

$$2\,KH_3(C_2O_4)_2 + 6\,NaOH = K_2C_2O_4 + 3\,Na_2C_2O_4 + 6\,H_2O,$$

and as a reducing agent:

$$KH_3(C_2O_4)_2 + 2\,MnO_2 + 3\,H_2SO_4 = 2\,MnSO_4 + KHSO_4 + 4\,CO_2 + 4\,H_2O.$$

(*a*) How many grams of the crystallized salt are contained in a liter when used as a standard N/10 acid solution? (*b*) As a reducing agent? *Ans.* (*a*) 8.472 g.
(*b*) 6.354 g.

419. A solution of sodium hydroxide containing 0.02003 g. per cubic centimeter is to be used in titrating sulphuric acid. What weight of the acid should be taken so that the reading of the burette in cubic centimeters shall equal the percentage of sulphuric acid in the sample? *Ans.* 2.4553 g.

420. A solution of potassium dichromate is equivalent to 0.00559 g. of iron per cubic centimeter. How many grams of

iron ore must be taken so that each cubic centimeter used in the determination shall indicate (*a*) 0.1% Fe? (*b*) 0.5% Fe?

Ans. (*a*) 5.59 g.
(*b*) 1.118 g.

421. When phenol-phthalein is used as an indicator, potassium dichromate may be titrated with an acid:

$$H_2SO_4 + K_2Cr_2O_7 = KHCr_2O_7 + KHSO_4.$$

How many grams of potassium dichromate must be contained in a liter to make a normal solution? *Ans.* 147.10 g.

422. Potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3\,H_2O$, acts as a reducing agent:

$$10\,K_4Fe(CN)_6 + 2\,KMnO_4 + 8\,H_2SO_4 = 10\,K_3Fe(CN)_6 + 6\,K_2SO_4 + 2\,MnSO_4 + 8\,H_2O.$$

How much potassium ferrocyanide is contained in a cubic centimeter of the normal solution? *Ans.* .42235 g.

423. How much arsenic is shown by 12.00 cc. of N/20 iodine solution, the reaction being

$$As_2O_3 + 4\,I + 2\,H_2O = As_2O_5 + 4\,HI.$$

Ans. 0.022488 g.

424. To what weight of calcium oxide does 30.00 cc. of 0.1 N potassium permanganate correspond when the calcium has been separated as the oxalate, acidified and the oxalic acid titrated by potassium permanganate? *Ans.* 0.084105 g.

425. (*a*) How many grams of silver nitrate in a cubic centimeter of N/5 solution? (*b*) To how many grams of sodium chloride are 20.00 cc. of this solution equivalent?

Ans. (*a*) 0.033978 g.
(*b*) 0.2338 g.

426. According to the reaction:

$$NH_4CNS + AgNO_3 = NH_4NO_3 + AgCNS.$$

(*a*) What is the weight of ammonium sulpho cyanate in a cubic centimeter of a 0.1 N solution? (*b*) How many grams of silver are shown by 15.00 cc. of 0.1 N ammonium sulpho cyanate solution? *Ans.* (*a*) 0.007612 g.
(*b*) 0.1618 g.

427. What is the value in terms of manganese dioxide, of a cubic centimeter of an N/10 solution of ferrous sulphate acting as a reducing agent, the reaction being

$$2\,FeSO_4 + MnO_2 + 2\,H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2\,H_2O.$$

Ans. 0.004347 g.

428. Phosphoric acid may be determined by adding an excess of silver nitrate and sodium acetate, when the following reaction takes place:

$$H_3PO_4 + 3\,AgNO_3 + 3\,CH_3COONa = Ag_3PO_4 + 3\,NaNO_3 + 3\,CH_3COOH,$$

the acetic acid being titrated with barium hydroxide,

$$Ba(OH)_2 + 2\,CH_3COOH = Ba(CH_3COO)_2 + 2\,H_2O.$$

If 41.20 cc. of 0.1 N barium hydroxide are required to neutralize the acetic acid, how much phosphoric acid is present?

Ans. 0.13467 g.

429. Antimony may be determined by digestion with potassium iodide and hydrochloric acid, the iodine distilled over and collected in potassium iodide and titrated with sodium thiosulphate. The reactions are

$$KI + HCl = KCl + HI,$$
$$4\,HI + Sb_2O_5 = Sb_2O_3 + 2\,H_2O + 4\,I,$$
$$4\,I + 4\,Na_2S_2O_3 = 4\,NaI + 2\,Na_2S_4O_6.$$

If 30.25 cc. of thiosulphate are required to determine the iodine liberated, each cubic centimeter of which indicates 0.01282 g. of iodine, how much antimony is present? *Ans.* 0.18365 g.

430. A solution of sulphuric acid contains 0.004912 g. of acid per cubic centimeter. What is the factor to 0.1 N?

Ans. 1.0014.

431. A solution of sulphuric acid is standardized against a standard solution of approximately 0.5 N sodium hydroxide, the factor of which is 0.9992 to 0.5 N. 45.00 cc. of the sodium hydroxide solution are required to neutralize 44.70 cc. of the sulphuric acid solution. What is the factor of the sulphuric acid solution to 0.5 N? *Ans.* 1.006.

432. A solution of sodium hydroxide is to be standardized. 2.4530 g. of pure anhydrous sodium carbonate are weighed out and it requires 45.70 cc. of a solution of sulphuric acid for neutralization. 45.15 cc. of this solution of sulphuric acid require 44.90 cc. of the solution of sodium hydroxide. What is the normality of this solution of sodium hydroxide?

Ans. 1.018 N.

433. A solution of potassium permanganate is found to be equivalent to 0.005600 g. of iron per cubic centimeter. (*a*) What is its normality? (*b*) If 20.20 cc. of this solution are used in a determination, to how many cubic centimeters of 0.1 N solution is this amount equivalent? *Ans.* (*a*) 0.1003 N.
(*b*) 20.21 cc.

434. 45.00 cc. of hydrochloric acid (factor to 0.1 N = 0.9987) require 87.25 cc. of a solution of barium hydroxide for neutralization. (*a*) What is the normality of the barium hydroxide? (*b*) What is the factor to 0.05 N? (*c*) How many grams of barium hydroxide are present per cubic centimeter?

Ans. (*a*) 0.05151 N.
(*b*) 1.030.
(*c*) 0.004414 g.

435. The factor of a solution of sodium chloride is 1.007 to 0.1 N. 40.00 cc. of this solution are equivalent to 39.90 cc. of a solution of silver nitrate according to the reaction:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

(*a*) What is the factor of the solution of silver nitrate to 0.1 N? (*b*) How many grams per cubic centimeter does the silver nitrate solution contain? *Ans.* (*a*) 1.0095.
(*b*) 0.01715 g.

436. 0.2118 g. of arsenious oxide are weighed out to standardize solutions of iodine and thiosulphate, the reactions being

$$As_2O_3 + 4\,I + 2\,H_2O = As_2O_5 + 4\,HI,$$
$$2\,I + 2\,Na_2S_2O_3 = 2\,NaI + Na_2S_4O_6.$$

It requires 42.40 cc. of iodine to react with the arsenious oxide. (*a*) What is the normality of the iodine solution? (*b*) If 43.60

cc. of the thiosulphate solution are equivalent to 43.00 cc. of the iodine solution, what is the normality of the thiosulphate solution? *Ans.* (*a*) 0.1009 N.
(*b*) 0.09961 N.

437. A solution of sulphuric acid being precipitated with an excess of barium chloride gives 0.05841 g. of barium sulphate per cubic centimeter. (*a*) What is the normality of this solution? (*b*) What is the factor to half normal? (*c*) To how many cubic centimeters of half normal acid are 18.20 cc. of this solution equivalent? (*d*) If 2.5000 g. of sodium carbonate require 45.00 cc. of this solution of sulphuric acid for neutralization, what is the per cent of sodium carbonate in the sample?
Ans. (*a*) 0.5004 N.
(*b*) 1.001.
(*c*) 18.22.
(*d*) 47.73%.

438. How many grams of sodium thiosulphate, $Na_2S_2O_3 \cdot 5\,H_2O$ must be present in a liter of solution to make it N/20, the reaction being

$$2\,Na_2S_2O_3 + I_2 = 2\,NaI + Na_2S_4O_6.$$

Ans. 12.411 g.

439. Oxalic acid may be used as an acid and as a reducing agent. When used as an acid, the reaction may be symbolized:

$$H_2C_2O_4 + 2\,NaOH = Na_2C_2O_4 + 2\,H_2O.$$

As a reducing agent, the reaction may be typified:

$$H_2C_2O_4 + O = H_2O + 2\,CO_2.$$

How many grams of the crystallized oxalic acid, corresponding to the formula $H_2C_2O_4 \cdot 2\,H_2O$, must be taken per liter to prepare (*a*) a liter of a 0.1 N solution in which the oxalic acid acts as an acid? (*b*) To prepare a 0.5 N solution, the acid acting as a reducing substance? *Ans.* (*a*) 6.3025 g.
(*b*) 31.5125 g.

440. Potassium tetroxalate, $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2\,H_2O$, crystallizes well and may be used to prepare standard solutions.

(*a*) How many grams of this salt should be taken to make a liter of normal solution, the salt acting as an acid according to the reaction:

$$KHC_2O_4 \cdot H_2C_2O_4 + 3\,NaOH = KNaC_2O_4 + Na_2C_2O_4 + 3\,H_2O.$$

(*b*) If used as a reducing solution, how many grams should be taken per liter to make a normal solution, the reaction being symbolized:

$$KHC_2O_4 + 2\,O = KOH + H_2O + 4\,CO_2.$$

Ans. (*a*) 84.72 g.
(*b*) 63.5325 g.

441. Crude cream of tartar, $KHC_4H_4O_6$, is to be titrated with 0.4876 N NaOH solution. What weight of this substance must be taken for titration so that the burette reading shall indicate the percentage of $KHC_4H_4O_6$ directly?

$$KHC_4H_4O_6 + NaOH = KNaC_4H_4O_6 + H_2O.$$

Ans. 9.1737 g.

442. A sample of oxalic acid, $H_2C_2O_4 \cdot 2\,H_2O$, is to be titrated with 0.1095 N potassium permanganate:

$$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O.$$

What weight of the sample must be taken so that the burette reading multiplied by two shall give the percentage of $C_2H_2O_4 \cdot 2\,H_2O$? *Ans.* 0.3451 g.

443. Manganese is titrated with potassium permanganate in neutral solution according to the following reaction:

$$2\,KMnO_4 + 3\,MnSO_4 + 2\,H_2O = K_2SO_4 + 5\,MnO_2 + 5\,H_2SO_4.$$

(*a*) How many grams of potassium permanganate are contained in a normal solution according to this reaction? (*b*) How many grams of manganese are equivalent to a cubic centimeter of a tenth normal solution of potassium permanganate made up on this basis? (*c*) If the potassium permanganate is standardized for use in an acid solution, to how many grams of manganese per cubic centimeter is such a solution equivalent? (In acid

solution, two molecules of potassium permanganate liberate five available oxygen atoms.) *Ans.* (*a*) 52.6767 g.
(*b*) 0.0027465 g.
(*c*) 0.001648 g.

444. A silver nitrate solution is 0.1032 N. What weight of sample of a chloride must be taken so that each cubic centimeter of silver nitrate solution used in titration shall indicate one per cent of chlorine? *Ans.* 0.3659 g.

445. A sample containing iron is to be titrated with 0.2016 N potassium permanganate solution. (*a*) What weight of material should be weighed out for titration so that each cubic centimeter used shall show one per cent of metallic iron? (*b*) So that the burette reading multiplied by two shall give the percentage of iron as ferric oxide? *Ans.* (*a*) 1.1258 g.
(*b*) 0.8048 g.

446. How many cubic centimeters of a 1.093 N solution are equivalent to 42.82 cc. of a 1.047 N solution? *Ans.* 41.02 cc.

447. How many cubic centimeters of a 0.02534 N solution are equivalent to 13.47 cc. of a 0.1073 N solution?
Ans. 57.04 cc.

448. How many cubic centimeters of a solution whose factor to N/2 is 1.003 are equivalent to 19.42 cc. of a solution whose factor to N/5 is 0.9942? *Ans.* 7.70 cc.

449. How many cubic centimeters of a solution, the factor of which to N/10 is 0.9982, are equivalent to 15.94 cc. of a solution whose factor to N/2 is 0.9743? *Ans.* 79.63 cc.

450. (*a*) 30.00 cc. of a 0.5018 N solution of sulphuric acid neutralize 59.02 cc. of a solution of sodium hydroxide. What is the normality of the sodium hydroxide solution?
Ans. 0.2551 N.

451. (*b*) 50.00 cc. of a solution of sulphuric acid yield 2.9250 g. of barium sulphate. 30.00 cc. of this solution neutralize 61.20 cc. of a solution of sodium hydroxide. What is the normality of the sodium hydroxide solution? *Ans.* 0.2457 N.

452. Hydrogen peroxide is titrated with potassium permanganate according to the reaction:

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2O_2 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2.$$

25.60 cc. of the hydrogen peroxide solution decolorized 45.90 cc. of the potassium permanganate solution, the strength of which is 0.6432 N. How many grams of hydrogen peroxide are present per liter? *Ans.* 1.9614 g.

453. 3.0153 g. of a solution of hydrogen peroxide require 53.15 cc. of a solution of 0.09920 N potassium permanganate to produce the pink color. The reaction is

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2O_2 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2.$$

What is the percentage of hydrogen peroxide in this sample? *Ans.* 3.74%.

454. Bleaching powder is to be analyzed for available chlorine. 7.0920 g. are rubbed up with water and made up to one liter. Of this suspension, 50.00 cc. are taken, treated with an excess of potassium iodide, and the liberated iodine titrated with N/10 solution of sodium thiosulphate. The reaction is

$$Cl_2 + 2\,KI = 2\,KCl + I_2.$$

If 35.50 cc. of the thiosulphate solution are required, what is the percentage of available chlorine? *Ans.* 35.50%.

455. A sample of material containing pyrolusite (MnO_2) is treated with hydrochloric acid:

$$MnO_2 + 4\,HCl = MnCl_2 + Cl_2 + 2\,H_2O.$$

The chlorine is led into a solution of potassium iodide liberating iodine:

$$2\,KI + Cl_2 = 2\,KCl + I_2.$$

The iodine is determined by a solution of sodium thiosulphate:

$$I_2 + 2\,Na_2S_2O_3 = 2\,NaI + Na_2S_4O_6.$$

25.40 cc. of 0.1016 N thiosulphate solution are required. How much pyrolusite is present? *Ans.* 0.1122 g.

456. (*a*) What is the equivalent in 0.5 N solution of 35.00 cc. of 0.1052 N solution? (*b*) How many cubic centimeters of 0.2 N solution are equivalent to 42.00 cc. of a 0.5063 N solution?

Ans. (*a*) 7.364 cc.
(*b*) 106.3 cc.

457. Manganese dioxide is reduced with an excess of oxalic acid (50.00 cc. of 0.2016 N):

$$MnO_2 + H_2SO_4 + C_2H_2O_4 = MnSO_4 + 2\,CO_2 + 2\,H_2O.$$

The excess of oxalic acid requires 10.15 cc. of 0.2008 N potassium permanganate:

$$2\,KMnO_4 + 5\,C_2H_2O_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O.$$

How much manganese dioxide is present? *Ans.* 0.3495 g.

458. 5.0000 g. of ammonium sulphate are treated in a flask with 100.00 cc. of sodium hydroxide solution (factor to 1 N = 1.009). After boiling till all the ammonia is expelled, the solution is titrated with sulphuric acid, 30.25 cc. (factor to 1 N = 1.002) being required. What is the percentage of ammonia (NH_3) indicated? *Ans.* 24.04%.

459. One cubic centimeter of a potassium permanganate solution is equivalent to 0.005000 g. of iron. To 40.00 cc. of the permanganate solution an excess of potassium iodide is added which causes a liberation of iodine according to the reaction:

$$2\,KMnO_4 + 10\,KI + 16\,HCl = 12\,KCl + 8\,H_2O + 2\,MnCl_2 + 10\,I.$$

The free iodine is titrated with a solution of sodium thiosulphate,

$$2\,Na_2S_2O_3 + 2\,I = 2\,NaI + Na_2S_4O_6,$$

35.90 cc. of the thiosulphate being required. What is the normality of the thiosulphate solution? *Ans.* 0.09977 N.

460. 2.1200 g. of pure anhydrous sodium carbonate are weighed out and treated with 50.00 cc. of a solution of sulphuric acid:

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2.$$

The excess of acid is titrated back with sodium hydroxide solution, 10.05 cc. being required:

$$H_2SO_4 + 2\,NaOH = Na_2SO_4 + 2\,H_2O.$$

The solution of sulphuric acid and the sodium hydroxide solution are titrated against each other when it is found that 45.00 cc. of the sulphuric acid solution require 45.10 cc. of sodium hydroxide for neutralization. If the sodium hydroxide solution is used for determining oxalic acid ($C_2H_2O_4 \cdot 2\,H_2O$), how many grams of oxalic acid are indicated by one cubic centimeter of the sodium hydroxide solution?

$$H_2C_2O_4 + 2\,NaOH = Na_2C_2O_4 + 2\,H_2O.$$

Ans. 0.06286 g.

461. Sulphur dioxide is determined by adding an excess of iodine (50.00 cc. of 0.1009 N):

$$Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2\,HI,$$

the excess of iodine being titrated back with sodium thiosulphate (20.15 cc. of 0.1022 N):

$$2\,Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2\,NaI.$$

How much sulphur dioxide is present? *Ans.* 0.09566 g.

462. One gram of a sample of nitrate of soda is examined by treating with Devada's alloy (which produces nascent hydrogen when acted upon by sodium hydroxide) which reduces the nitrate to ammonia. The ammonia is collected in 100.00 cc. of 0.1157 N sulphuric acid. 10.15 cc. of 0.1063 N sodium hydroxide are necessary to neutralize the excess of sulphuric acid. What is the per cent of sodium nitrate in the sample?

Ans. 89.18%.

463. Potassium persulphate is estimated by potassium permanganate indirectly. When treated with a ferrous salt in acid solution:

$$K_2S_2O_8 + 2\,FeSO_4 = Fe_2(SO_4)_3 + K_2SO_4,$$

the excess of ferrous sulphate being determined by permanganate:

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O.$$

30.00 cc. of the ferrous sulphate solution are equivalent to 31.25 cc. of 0.1000 N $KMnO_4$ solution. 30.00 cc. of the ferrous sulphate solution together with the sample of potassium persulphate require 7.35 cc. of 0.1000 N potassium permanganate solution. How much potassium persulphate is present?

Ans. 0.3230 g.

464. Iodine in iodides is determined by adding an excess of silver nitrate:

$$KI + AgNO_3 = AgI + KNO_3,$$

and the excess of silver nitrate is found with potassium thiocyanate:

$$AgNO_3 + KCNS = KNO_3 + AgCNS.$$

42.00 cc. of silver nitrate solution are equivalent to 40.15 cc. of thiocyanate solution. 1.00 cc. of the silver nitrate solution contains 0.010820 g. of silver. How much potassium iodide is indicated if 32.00 cc. of the silver nitrate solution were added and 2.80 cc. of the thiocyanate solution were required for the back titration? *Ans.* 0.4841 g.

465. Iron in the ferric condition is treated with an excess of sodium thiosulphate (50.00 cc.):

$$2\,Na_2S_2O_3 + 2\,FeCl_3 + 2\,HCl = 2\,FeCl_2 + 4\,NaCl + H_2S_4O_6.$$

The excess of thiosulphate is found to require 7.85 cc. of iodine solution. The solution of iodine was standardized by titrating it against a standard arsenic solution, each cubic centimeter of which contained 0.005162 g. of arsenious oxide:

$$As_2O_3 + 2\,I_2 + 2\,H_2O = As_2O_5 + 4\,HI,$$

45.00 cc. of the arsenic solution requiring 45.20 cc. of the iodine solution. The thiosulphate solution was standardized by titrating it against the iodine solution:

$$I_2 + 2\,Na_2S_2O_3 = 2\,NaI + Na_2S_4O_6,$$

45.00 cc. of the iodine solution requiring 45.95 cc. of the thiosulphate solution. What is the weight of iron present?

Ans. 0.2385 g.

466. A solution of sodium carbonate and bicarbonate is to be examined for the content of these salts. Phenol-phthalein is added and the solution titrated with 0.1000 N hydrochloric acid in the cold, requiring 30.00 cc. Phenol-phthalein reacts neutral when all the carbonate is converted to bicarbonate:

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

Methyl orange is added which reacts acid when all the bicarbonate is decomposed:

$$NaHCO_3 + HCl = NaCl + CO_2 + H_2O,$$

35.00 cc. more being required. What are the amounts of carbonate and bicarbonate of soda present?

Ans. 0.3180 g. Na_2CO_3,
0.0420 g. $NaHCO_3$.

467. A sample of quicklime is to be analyzed for calcium oxide and calcium carbonate. 14.0000 g. are weighed out, slaked with warm water (free from carbon dioxide) and made up to 500 cc. Of this emulsion, 50 cc. are pipetted out and again made up to 500 cc., 50.00 cc. of this latter solution being taken for analysis. 60.00 cc. of N/10 hydrochloric acid solution are added and the whole heated to boiling or till there is no further evolution of carbon dioxide.

$$Ca(OH)_2 + 2\,HCl = CaCl_2 + 2\,H_2O,$$
$$CaCO_3 + 2\,HCl = CaCl_2 + H_2O + CO_2.$$

The excess of acid is found by titrating back with N/10 sodium hydroxide solution, 20 cc. being required, methyl orange being used as an indicator. A second portion of 50 cc. is taken and titrated with N/10 hydrochloric acid solution, using phenol-phthalein as an indicator, 35 cc. being required. Under these conditions only the calcium hydroxide is titrated. Calculate the percentages of calcium oxide and calcium carbonate in the quicklime.

Ans. 70.09% CaO,
17.87% $CaCO_3$.

468. 1.5000 g. of iron are dissolved in hydrochloric acid and treated with 0.7300 g. of a nitrate.

$$2\,MNO_3 + 6\,FeCl_2 + 8\,HCl = 2\,MCl + 2\,NO + 6\,FeCl_3 + 4\,H_2O.$$

After reaction, the excess of ferrous chloride is determined by titration with N/2 potassium permanganate.

$$2\,KMnO_4 + 10\,FeCl_2 + 16\,HCl = 2\,KCl + 2\,MnCl_2 + 10\,FeCl_3 + 8\,H_2O.$$

An independent determination shows that 1.5000 g. of iron require 53.55 cc. of the N/2 potassium permanganate solution. The excess of ferrous chloride requires 3.55 cc. of the permanganate solution. (*a*) If the nitrate taken is sodium nitrate ($NaNO_3$), calculate the percentage present. (*b*) The percentage of N_2O_5. *Ans.* (*a*) 97.05% $NaNO_3$, (*b*) 61.66% N_2O_5.

469. Phenol-phthalein is neutral to acid sodium carbonate. By using methyl orange, the acid sodium carbonate may be titrated to completion, *i.e.*, to sodium chloride, carbon dioxide and water. A sample of sodium carbonate containing sodium hydroxide is titrated with hydrochloric acid (factor to 0.1 N = 0.9985) using phenol-phthalein, when 50.00 cc. are required. Methyl orange is added and 20.00 cc. more hydrochloric acid are needed to produce acid reaction with this indicator. What are the amounts of sodium hydroxide and sodium carbonate present? *Ans.* 0.1198 g. NaOH, 0.2117 g. Na_2CO_3.

470. Calculate the composition of a mixed acid from the following:

For total acid:

Weight of acid taken	4.8970 g.
NaOH to neutralize	81.60 cc.

For H_2SO_4 (other acids being driven off by evaporation):

Weight of acid taken	8.5420 g.
NaOH to neutralize	80.75 cc.

For N_2O_3:

Weight of acid taken	17.000 g.
0.1 N $KMnO_4$ required	10.00 cc.

Factor NaOH solution to normal is 1.039.

Ans. $H_2SO_4 = 48.17\%$,
$HNO_3 = 47.03\%$,
$N_2O_3 = 0.11\%$,
$H_2O = 4.69\%$,
100.00%.

471. Calculate the composition of a mixed acid from the following:

For total acid:

Weight of acid taken	5.9216 g.
1.012 N NaOH to neutralize	99.92 cc.

For H_2SO_4 (other acids being driven off by evaporation):

Weight of acid taken	10.4387 g.
1.012 N NaOH to neutralize	104.00 cc.

For N_2O_3:

Weight of acid taken	18.000 g.
0.1 N $KMnO_4$ required	9.00 cc.

Ans. $H_2SO_4 = 49.45\%$,
$HNO_3 = 43.92\%$,
$N_2O_3 = 0.10\%$,
$H_2O = 6.53\%$,
100.00%.

472. Let

x = percentage of free acetic anhydride $(C_2H_3O)_2O$,
y = percentage of total acidity calculated to acetic anhydride.

Derive the formula

$$x = 6.6643\,(y - 84.995).$$

473. One gram of a sample of acetic anhydride containing acetic acid was treated with 200 cc. of a solution of barium hydroxide.

$$(C_2H_3O)_2O + H_2O = 2\,CH_3COOH,$$
$$Ba(OH)_2 + 2\,CH_3COOH = Ba(C_2H_3O_2)_2 + 2\,H_2O.$$

200.00 cc. of the barium hydroxide solution was found to be equivalent to 190.00 cc. of an N/10 solution of hydrochloric acid. The excess of barium hydroxide was titrated back with N/10 hydrochloric acid, 1.37 cc. being required. What are the percentages of acetic anhydride and acetic acid present?[1]

Ans. 74.99% $(C_2H_3O)_2O$,
25.01% CH_3COOH.

474. 0.8585 g. of a sample of acetic anhydride containing acetic acid is treated with 200.00 cc. of a solution of barium hydroxide. This volume of barium hydroxide solution is equivalent to 170.00 cc. of N/10 hydrochloric acid. The excess of barium hydroxide is titrated back with N/10 hydrochloric acid, 8.46 cc. being required. Calculate the percentages of acetic anhydride and acetic acid present in this sample. (See the two problems above.) *Ans.* 73.41% $(C_2H_3O)_2O$,
26.59% CH_3COOH.

475. Sodium hydroxide and trisodium phosphate are to be determined in the presence of each other. Phenol-phthalein reacts neutral to disodium phosphate; therefore, in titrating a mixture of these two salts with sulphuric acid and phenol-phthalein:

$$2x\,NaOH + 2y\,Na_3PO_4 + (x+y)\,H_2SO_4 = 2y\,Na_2HPO_4 + (x+y)\,Na_2SO_4 + 2x\,H_2O.$$

45.00 cc. of 0.5000 N H_2SO_4 are required for this titration. Methyl orange is now added, which is alkaline toward disodium phosphate, but neutral to monosodium phosphate. The titration is continued with 0.5000 N H_2SO_4:

$$2y\,Na_2HPO_4 + y\,H_2SO_4 = 2y\,NaH_2PO_4 + y\,Na_2SO_4,$$

35.00 cc. being required. What are the amounts of trisodium phosphate and sodium hydroxide? *Ans.* 0.2000 g. NaOH,
2.8707 g. Na_3PO_4.

476. (For the conduct of the sodium salts of phosphoric acid with indicators, see problem 475.) What is the composition of a solution of mixed tri and disodium phosphate if the phenol-

[1] See problem above; also note similar case of oleum, p. 191.

[illegible] titration required 25.00 cc. of 1.5000 N H_2SO_4 and the titration with methyl orange required 35.00 cc. 1.5000 N H_2SO_4 in addition.

Ans. 1.705 g. Na_2HPO_4
2.555 g. Na_3PO_4

477. Oleum often contains sulphur dioxide. When the sample is dissolved in water and titrated with standard sodium hydroxide solution, using phenol-phthalein, the sulphur dioxide combines with the water, forming sulphurous acid, which takes up sodium hydroxide:

$$H_2SO_3 + 2\,NaOH = Na_2SO_3 + 2\,H_2O.$$

What is the analysis of an oleum from the following data:

For total acid as SO_3:

Weight of oleum taken	3.0570 g.
1 N NaOH required	74.30 cc.

For sulphur dioxide:

Weight of oleum taken	7.0510 g.
0.1 N I solution required	46.50 cc.

The reaction for the sulphurous acid and iodine is

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2\,HI.$$

Ans. Free SO_3 = 80.31%,
H_2SO_4 = 17.56%.
SO_2 = 2.13%.
100.00%.

478. What is the composition of an oleum titrated with phenol-phthalein as an indicator, giving the following:

For total acid:

Weight of acid taken	5.0000 g.
1.112 N NaOH to neutralize	99.95 cc.

For sulphur dioxide:

Weight of acid taken	5.0000 g.
0.1 N I solution required	39.00 cc.

Ans. Free SO_3 = 34.17%,
H_2SO_4 = 63.33%,
SO_2 = 2.50%.

479. A solution shows 0.049205 g. of sulphuric acid per cubic centimeter. How many cubic centimeters of water must be added to a kilogram of this solution to make it 1.000 N?

Ans. 3.20 cc.

480. How much 0.2019 N sodium hydroxide and water must be taken to make 5 liters of 0.1000 N sodium hydroxide?[1]

Ans. 2391.2 cc. NaOH,
2608.8 cc. H_2O.

481. 50.00 cc. of a solution (factor to N/10 = 1.005) correspond to 48.90 cc. of another solution. How many cubic centimeters of water per liter must be added to this second solution to make it N/10? *Ans.* 28.00 cc.

482. How many grams each of a 0.5012 N solution must be mixed with a 0.1078 N solution to make one kilogram of a 0.2000 N solution? *Ans.* 765.6 g. 0.1078 N,
234.4 g. 0.5012 N.

483. How many pounds of 80.00% acetic acid must be added to 92.60% acetic acid to make 600 lbs. of 90.00% acetic acid?

Ans. 123.8 lbs. 80.00%,
476.2 lbs. 92.60%.

484. How many pounds of water and how many pounds of 60.00% sulphuric acid must be mixed to prepare 400 lbs. of a 34.20% sulphuric acid? *Ans.* 288 lbs. 60% H_2SO_4,
172 lbs. water.

485. How many pounds of water must be added to 800 pounds of 73.00% sulphuric acid to make the whole 70.00% sulphuric acid? *Ans.* 34.29 lbs. water.

486. How much water must be added to 1000 cc. of a 0.1128 N solution to make it 0.1000 N? (When the densities of the solutions mixed, and the density of the resultant solution are very nearly the same, as in this case, volumes may be substituted in the formulas without sensible error.)

Ans. 128.00 cc. water.

[1] Consider the densities of the two liquids and the resultant to be the same in this, and in other similar problems, unless otherwise mentioned.

487. How many pounds of 62.18% sulphuric acid and of 98.00% sulphuric acid must be taken to make 1000 lbs. of 93.00% acid? *Ans.* 139.6 lbs. 62.18% H_2SO_4, 860.4 lbs. 98.00% H_2SO_4.

488. How many pounds of 62.18% sulphuric acid must be added to 1000 lbs. of 98.00% sulphuric acid to dilute the whole to 93.00% acid? *Ans.* 162.2 lbs. 62.18% H_2SO_4.

489. How much 0.1012 N solution must be added to 1000 cc. of a 0.5009 N solution to make it 0.2000 N?

Ans. 3045.5 cc. 0.1012 N.

490. How many pounds of 80.00% acetic acid and 60.00% acetic acid should be mixed to make 500 lbs. of 65.00% acetic acid?[1] *Ans.* 125 lbs. 80% CH_3COOH, 375 lbs. 60% CH_3COOH.

491. How many cubic centimeters of 0.0957 N and 0.1120 N solution must be taken to make 1000 cc. of 0.1000 N solution? (Consider the 0.0957 N solution as being strengthened by the 0.1120 N solution.) *Ans.* 263.8 cc. 0.1120 N, 736.2 cc. 0.0957 N.

492. How many pounds of 80.00% sulphuric acid must be added to 980 lbs. of 35.00% sulphuric acid to strengthen the whole to 40.00% acid? *Ans.* 122.5 lbs. 80% H_2SO_4.

493. How many pounds of a 20.00% hydrochloric acid must be added to 800 lbs. of a 43.00% hydrochloric acid to convert this weight into a 30.00% hydrochloric acid?

Ans. 1040 lbs.

494. How many pounds each of a 30.00% oleum and a 98.00% sulphuric acid must be mixed to prepare 100 lbs. of 100.00% sulphuric acid? (Calculate the percentages of SO_3 present in each.) *Ans.* 22.82 lbs. 30.00% oleum, 77.18 lbs. 98.00% H_2SO_4.

[1] In a problem of this kind in which a definite amount is called for, (*a*) of formula II of page 227 serves as well as (*a*) of formula III. In one case the formula gives the amount of diluting solution to add; in the other, the amount of strengthening solution required.

CHAPTER X

USE OF SPECIFIC GRAVITY TABLES AND ACID CALCULATIONS

Calculation of Data in Specific Gravity Tables. — Large shipments of acid, particularly sulphuric acid, are usually billed and paid for on the basis of 66° Bé., 60° Bé., etc. It is, therefore, necessary to calculate the actual strength of the acid to its equivalent in 66° Bé., or whatever the strength basis of the acid is billed and paid for.

The table of Ferguson and Talbot,[1] for sulphuric acid will be used as a model, the same serving as an example of the use of such data. The methods of calculation of the data will be explained, the same being applicable to other solutions, the tables of which have not been so fully arranged.[2]

Specific gravity tables do not represent individual determinations for the densities listed,[3] but are constructed from curves and methods of interpolation already considered.[4]

Twaddell's Hydrometers [5] consist of a series of hydrometers so arranged that the graduations permit of easy reading over a wide range. They are graduated only for

[1] See Appendix, also Chem. Ann., pp. 388–393.

[2] See Chem. Ann., pp. 392–456.

[3] The Baumé is given in Ferguson and Talbot's table to two significant figures; it is accurate to two places of decimals.

[4] Pp. 32–41.

[5] See table of Ferguson and Talbot, Chem. Ann., pp. 388–392, column 3.

liquids heavier than water. The unit of the Twaddell scale is 0.005 specific gravity; hence if X is the reading Twaddell,

$$\text{Sp. gr.} = 1 + 0.005\,X.$$

The weight of a cubic foot of water at 60° F. is 62.37 pounds. The weight of a cubic foot of a liquid is its specific gravity multiplied by 62.37.[1]

The acid content corresponding to 66° Bé. (Oil of Vitriol, O. V.) has been carefully ascertained and found to be 93.19% H_2SO_4. A sample of sulphuric acid of 65.75° Bé. containing 91.80% H_2SO_4[2] is equivalent to

$$\frac{91.80}{93.19} \times 100 = 98.51\%\ \text{O. V.},^{3}$$

and as a cubic foot of liquid of 65.75° Bé., which is equivalent to 1.8297 sp. gr., weighs 114.12 lbs. (62.37 × 1.8297),[4] the number of pounds of Oil of Vitriol equivalent to one cubic foot of this acid is

$$\frac{91.80}{93.19} \times 114.12 = 112.42\ \text{lbs.}^{5}$$

The equivalent in 60° Bé. acid (77.67% H_2SO_4) of an acid of 64° Bé. (85.66% H_2SO_4) is

$$\frac{85.66}{77.67} \times 100 = 110.29\%,^{6}$$

[1] See table of Ferguson and Talbot, Chem. Ann., pp. 388–392, column 3.

[2] *Ibid.*, p. 392, column 4.

[3] *Ibid.*, p. 392, column 6.

[4] *Ibid.*, p. 392, column 5.

[5] *Ibid.*, p. 392, column 7.

[6] *Ibid.*, p. 393, column 3.

and as 60° Bé. corresponds to 1.7059 sp. gr., the number of pounds of 60° Bé. equivalent to a cubic foot of 64° Bé. sulphuric acid is

$$\frac{85.66}{77.67} \times 1.7059 \times 62.37 = 123.14 \text{ lbs.}^{1}$$

Use of Specific Gravity Tables. — As an example illustrating the use to which specific gravity tables may be put, suppose it is required to calculate the number of pounds of 50° Bé. sulphuric acid in a shipment, the following data being given:

42 inches of sulphuric acid are drawn out of a tank at a temperature of 101° F. Suppose that it has been determined by calculating the capacity of the tank from the inside measurements; that 1 inch in the depth of the tank corresponds to 50.00 cubic feet. A sample of the acid taken from the tank and brought into the laboratory showed 56.88° Bé. at 92° F. Correction must be made for temperature in order to reduce to 60° F., the temperature for which the tables are constructed:

$$92° - 60° = 32° \text{ difference.}^{2}$$

From the table under the heading "Allowance for Temperature,"[3] it is seen that the allowance for 60° Bé. acid is 0.026° Bé. for each degree Fahrenheit, and that the correction for 50° Bé. acid is 0.028° Bé. As the acid in question is about midway between these points, the allowance for each degree Fahrenheit is very nearly 0.027° Bé. The correction for temperature is

$$32 \times 0.027 = 0.86° \text{ Bé.},$$

[1] See table of Ferguson and Talbot, Chem. Ann., p. 393, column 4; also from the product of the corresponding figure in column 5, p. 392, and the fraction given.

[2] *Ibid.*, p. 388, note to table.

[3] *Ibid.*, p. 391.

and as the standard temperature, 60° F., is lower than 92° F., the temperature at which the Baumé of the sample was taken, the acid becoming denser as the temperature is lowered, this amount must be added. The Baumé of the acid at 60° F. is then

$$\text{[illegible]} - 1.00 = \text{[illegible]}^\circ \text{ Bé. at } 60^\circ \text{ F.}$$

The Baumé of the acid at 101° F., the temperature at which the acid was drawn off, is calculated:

$$101 - 60 = 41^\circ \text{ F. difference.}$$
$$41 \times 0.025^{1} = 1.03^\circ \text{ Bé. correction.}$$

and as the density of the acid is lowered as the temperature is raised,

$$\text{[illegible]} - 1.03 = 50.03^\circ \text{ Bé. at } 101^\circ \text{ F.}$$

The easiest way to get the specific gravity corresponding to this degree Baumé is by interpolating the given data.

$$50^\circ \text{ Bé.} = 1.5417 \text{ sp. gr.}$$
$$50^\circ \text{ Bé.} = 1.6292 \text{ sp. gr.}$$
$$\text{diff.} = 0.0125 \text{ sp. gr.}$$
$$50.03 - 50.00 = 0.03^\circ \text{ Bé. diff.}$$
$$0.0125 \times 0.03 = 0.0017 \text{ sp. gr.}$$

$1.6292 - 0.0017 = 1.6409$ sp. gr. corresponding to 50.03° Bé. Then, as 42 inches were drawn from the tank, the pounds drawn off are

$$42 \times 50.00 \times 12.37 \times 1.6409 = 214.29 \text{ lbs.}$$

As the acid is sold on the basis of 50° Bé., the pounds of 50° Bé. corresponding to 50.03° Bé. must be easily found by interpolating from the table

[1] See table of Ferguson and Talbot, Chem. Ann., p. 88, column 2.

58° Bé. = 119.59% 50° Bé. acid[1]
57° Bé. = 117.00% 50° Bé. acid
diff. = 2.59% 50° Bé. acid,
$2.59 \times 0.74 = 1.92$,
$117 + 1.92 = 118.92\%$ 50° Bé. acid corresponding to 57.74° Bé. acid,
$214{,}920 \times 1.1892 = 255{,}827$ lbs. 50° Bé. acid.

Calculation of Mixed Acid. — "Mixed Acid" is a commercial term, generally meaning a mixture of nitric and sulphuric acids, and is extensively used in manufacturing processes. On account of the relative costs of concentrated and dilute nitric acids, the water called for is added in the form of dilute nitric acid, using a minimum of concentrated nitric acid and a maximum of dilute nitric acid. Water, as such, is seldom added. For example, let it be required to calculate the quantities of acids necessary to make a mixture ("mix") of 60,000 lbs. of a mixed acid to consist of

	Per cent
H_2SO_4 (add as 98% H_2SO_4)	46.00
HNO_3 (add as 61.4% and as 95.5% HNO_3)	49.00
H_2O	5.00
	100.00

$60{,}000 \times 0.46 = 27{,}600$ lbs. H_2SO_4 called for
$60{,}000 \times 0.49 = 29{,}400$ lbs. HNO_3 called for
$60{,}000 \times 0.05 = 3{,}000$ lbs. H_2O called for
60,000 lbs.

$$\frac{27{,}600}{0.98} = 28{,}163 \text{ lbs. } 98\% \ H_2SO_4 \text{ to take,}$$

$60{,}000 - 28{,}163 = 31{,}837$ lbs. still to add.

[1] See table of Ferguson and Talbot, Chem. Ann., p. 391, column 5.

Let x = number of pounds of 95.5% HNO_3 to add; then 31,837 − x will represent the number of pounds of 61.4% HNO_3 to add. By algebra:

$$0.955\,x + 0.614\,(31{,}837 - x) = 29{,}400.$$

Solving:

$$x = 28{,}891 \text{ lbs. } 95.5\%\ HNO_3 \text{ to take,}$$
$$31{,}837 - 28{,}891 = 2946 \text{ lbs. } 61.4\%\ HNO_3 \text{ to take.}$$

So, to make the mix, take

H_2SO_4	28,163 lbs. 98%
HNO_3	28,891 lbs. 95.5%
HNO_3	2,946 lbs. 61.4%
	60,000 lbs.

This same result might have been reached by means of the formulas given to adjust the strengths of liquids.[1] 29,400 lbs. of 100% nitric acid are called for; the weight of material still to be added, after the 98% sulphuric acid is added, is 31,837 lbs. as before. This makes

$$\frac{29{,}400}{31{,}837} \times 100 = 92.35\%\ HNO_3 \text{ to be added.}$$

To make 31,837 lbs. of an acid of this concentration from 95.5% and 61.4% nitric acid, using III (*a*) of page 227,

$$\frac{92.35 - 61.4}{95.50 - 61.4} \times 31{,}837 = 28{,}896 \text{ lbs. } 95.5\%\ HNO_3 \text{ to take, as before.}$$

$$31{,}837 - 28{,}896 = 2941 \text{ lbs. } 61.4\%\ HNO_3 \text{ to take, as before.}$$

Strengthening a Mixed Acid by Means of Oleum.— An example involving the use of oleum will next be considered. Let it be required to make 61,320 lbs. of a mixed acid of the composition:

[1] Pp. 227–228, II (*a*), or III (*a*), according to whether the acid is regarded as being diluted or strengthened.

	Per cent
HNO_3 (add as 94.5% HNO_3)	56.00
H_2SO_4 (add as 98.56% H_2SO_4 and as 20.00% oleum, a minimum of which is to be taken)	41.00
H_2O	3.00
	100.00

The tank in which the acid is to be mixed already contains 2604 lbs. of the remains of a previous mix of the composition:

	Per cent
HNO_3	52.00
H_2SO_4	42.50
H_2O	5.50
	100.00

Consequently,

	H_2SO_4	HNO_3	H_2O
	Lbs.	Lbs.	Lbs.
Called for	25,141	34,339	1840
In tank	1,107	1,354	143
To be added	24,034	32,985	1697

If the attempt were made to calculate the weights of acid to add by the previous method, it would be seen that the method would not work, as too much water would be added with the sulphuric acid and, hence, a nitric acid stronger than 94.5% HNO_3 would have to be used to complete the mix; hence, oleum will have to be employed. Thus:

$$\frac{24{,}034}{0.9856} = 24{,}385 \text{ lbs. } 98.56\% \ H_2SO_4,$$

$24{,}385 - 24{,}034 = 351$ lbs. H_2O added with the 98.56% H_2SO_4,

$1697 - 351 = 1346$ lbs. H_2O remaining.

Adding this water with the nitric acid would call for a stronger nitric acid than the 94.5% HNO_3, as is seen from the following:

$$32{,}985 + 1346 = 34{,}331 \text{ lbs. } HNO_3 \text{ and } H_2O \text{ still to add,}$$

$$\frac{32{,}985}{34{,}331} \times 100 = 96.08\% \ HNO_3 \text{ required to complete the mix.}$$

Going back to the original figures after this preliminary calculation which has shown the necessity of using oleum; first calculating the weight of nitric acid to be added:

$$\frac{32{,}985}{0.945} = 34{,}905 \text{ lbs. } 94.5\% \ HNO_3 \text{ to add,}$$

$34{,}905 - 32{,}985 = 1920$ lbs. H_2O added with the 94.5% HNO_3.

But the mix only calls for 1697 lbs. of water, hence 1920 − 1697 = 223 lbs. of water will be added in excess. This water must be taken up with oleum. Now, to the acid already in the tank the following quantities of acid must be added:

H_2SO_4	24,034 lbs. 100% H_2SO_4
HNO_3	32,985 lbs. 100% HNO_3
H_2O	1,697 lbs. 100% H_2O
Total	58,716

In adding 34,905 lbs. of 94.5% HNO_3 there remain only 58,716 − 34,905 = 23,811 lbs. of acid (H_2SO_4) to add. To adjust the proportions and not add more acid than called for is done by adding oleum which takes up water from the nitric acid. The percentage strength of the sulphuric acid requisite is

$$\frac{24{,}034}{23{,}811} \times 100 = 100.93\% \ H_2SO_4.$$

The percentage of SO_3 in 100.93% H_2SO_4 is

$$\frac{SO_3}{H_2SO_4} = \frac{80.07}{98.09} \times 100.93 = 82.39\% SO_3;$$

in 98.56% H_2SO_4 the percentage of SO_3 is

$$\frac{SO_3}{H_2SO_4} = \frac{80.07}{98.09} \times 98.56 = 80.45\% SO_3;$$

in 20.00% oleum the percentage of SO_3 is[1]

Per cent $SO_3 = 0.8163\ (100 - 20) + 20 = 85.31\%\ SO_3$;

then, to make 23,811 lbs. of a 100.93% H_2SO_4, from 20.00% oleum and 98.56% H_2SO_4, require:[2]

$$\frac{82.39 - 80.45}{85.31 - 80.45} \times 23{,}811 = 9506 \text{ lbs. } 20\% \text{ oleum},$$

$$23{,}811 - 9506 = 14{,}305 \text{ lbs. } 98.56\%\ H_2SO_4.$$

So, to make the mix, add to the acid already in the tank:

HNO_3	34,905 lbs. 94.50%
H_2SO_4	14,305 lbs. 98.56%
Oleum	9,506 lbs. 20.00%

It is frequently desired to prepare a "mix" from a mixed acid already on hand by adding to it the requisite amounts of sulphuric acid and nitric acid to bring it up to the desired concentration. Thus, it may be required to fortify a "spent" mixed acid, or it may be that after adding the calculated amounts of ingredients to make a batch of mixed acid that the mixed acid resulting does not analyze up to specifications. It must then be adjusted by a further addition of the deficient constituent. Thus, suppose a mixed acid of the following composition is desired:

	Per cent
H_2SO_4	46.00
HNO_3	49.00
H_2O	5.00

[1] See p. 191.

[2] See p. 228.

and there is on hand a supply of mixed acid of the composition:

	Per cent
H_2SO_4	45.10
HNO_3	48.00
H_2O	6.90

How many pounds of 98% sulphuric acid and 96% nitric acid should be added to the mixed acid for each 1000 lbs. of the corrected acid produced? An algebraic method of calculation is as follows:

Let x = weight of mixed acid to take,
y = weight of 98% H_2SO_4 to take,
z = weight of 96% HNO_3 to take.

The total sulphuric acid in the corrected mix must be

$(0.451)\,x$ = weight of H_2SO_4 added with the mixed acid,
$(0.98\ )\,y$ = weight of H_2SO_4 added as 98% H_2SO_4.

The total nitric acid in the corrected mix must be

$(0.48)\,x$ = weight of HNO_3 added with the mixed acid,
$(0.96)\,z$ = weight of HNO_3 added as 96% HNO_3.

The total water in the corrected mix must be

$(0.069)\,x$ = weight of H_2O added with the mixed acid,

$(1.00 - 0.98)\,y = (0.02)\,y$ = weight of H_2O added with the 98% H_2S_4O,

$(1.00 - 0.96)\,z = (0.04)\,z$ = weight of H_2O added with the 96% HNO_3 acid.

In each 1000 lbs. of the corrected mix there must be

$1000 \times 0.46 = 460$ lbs. H_2SO_4,
$1000 \times 0.49 = 490$ lbs. HNO_3,
$1000 \times 0.05 = 50$ lbs. H_2O.

Hence, the following equations result:

$$\begin{aligned}
&(1) \quad (0.451)\,x + (0.98)\,y \qquad\qquad = 460.\\
&(2) \quad (0.48)\;\; x \qquad\qquad + (0.96)\,z = 490.\\
&(3) \quad (0.069)\,x + (0.02)\,y + (0.04)\,z = \;\; 50.
\end{aligned}$$

Expressing (1) and (2) in terms of x by solving for y and z in these equations:

$$(4) \quad y = \frac{460-(0.451)\,x}{0.98} = \frac{460}{0.98} - \frac{(0.451)\,x}{0.98}$$
$$= 469.388 - (0.460204)\,x.$$

$$(5) \quad z = \frac{490 - (0.48)\,x}{0.96} = \frac{490}{0.96} - \frac{(0.48)\,x}{0.96}$$
$$= 510.417 - (0.500000)\,x.$$

Substituting in (3) gives

$$\begin{aligned}
&(0.069)\,x + 0.02\,[469.388 - (0.460204)\,x]\\
&\qquad + 0.04\,[510.417 - (0.500000)\,x] = 50,\\
&(0.069)\,x + 9.38776 - (0.00920408)\,x\\
&\qquad + 20.41668 - (0.02)\,x = 50,\\
&(0.03979512)\,x = 20.19556,\\
&x = \frac{20.19556}{0.03979512} = 507.49 \text{ lbs. mixed acid to take per 1000 lbs.}
\end{aligned}$$

Substituting this value of x in (4) and (5) gives

$$y = 469.388 - (0.460204)\;(507.49) = 235.84 \text{ lbs. } 98\%\ H_2SO_4 \text{ to take,}$$

$$z = 510.417 - (0.500000)\;(507.49) = 256.67 \text{ lbs. } 96\%\ HNO_3 \text{ to take.}$$

The ratios of these values may be used either to prepare a definite amount of mixed acid or to correct a definite amount of "spent" acid. Knowing the ratios per 1000 lbs. the quantities requisite for any weight of acid are readily calculated. After making a calculation, it is

often a good plan to check up the results. This insures the accuracy of the calculation. Thus in the above calculation:

	H_2SO_4	HNO_3	H_2O
	Lbs.	Lbs.	Lbs.
Mixed acid	228.88	243.60	35.01
98% H_2SO_4	231.12	.....	4.72
96% HNO_3	.....	246.40	10.27
	460.00	490.00	50.00

PROBLEMS

498. What is the Twaddell reading corresponding to (*a*) 1.6117 sp. gr.? (*b*) To 66.00° Bé.? *Ans.* (*a*) 122.2 Tw., (*b*) 167.1 Tw.

499. What is the reading of 141.2 Tw. in (*a*) specific gravity and (*b*) in Baumé? *Ans.* (*a*) 1.7060 sp. gr., (*b*) 60.00° Bé.

500. (*a*) What is the percentage O. V. (Oil of Vitriol, 93.19% H_2SO_4) equivalent to 62.18% H_2SO_4? (*b*) What is the percentage of 50° Bé. sulphuric acid (62.18% H_2SO_4) equivalent to O. V.? *Ans.* (*a*) 66.72%, (*b*) 149.87%.

501. (*a*) What is the equivalent in Oil of Vitriol (93.19% H_2SO_4) of 600 lbs. of a sulphuric acid of 89.55% H_2SO_4? (*b*) In 50° Bé. sulphuric acid (62.18% H_2SO_4)? *Ans.* (*a*) 576.6 lbs., (*b*) 864.12 lbs.

502. Find the percentage of 100% H_2SO_4 equivalent to (*a*) a 20.00% oleum? (*b*) To a 30.00% oleum? *Ans.* (*a*) 104.5%, (*b*) 106.75%.

503. What is the percentage of Oil of Vitriol equivalent to 25.00% oleum? (*b*) What is the percentage of 98.00% sulphuric acid equivalent to a 35.00% oleum?

Ans. (*a*) 113.34%, (*b*) 110.08%.

504. Knowing that 60° Bé. sulphuric acid contains 77.67% H_2SO_4 and that 50° Bé. sulphuric acid contains 62.18% H_2SO_4, what is the number of pounds of 50° Bé. sulphuric acid equivalent to a cubic foot of 60° Bé. sulphuric acid?

Ans. 132.91 lbs.

505. 50° Bé. sulphuric acid contains 62.18% H_2SO_4, and 52° Bé. sulphuric acid contains 65.13% H_2SO_4. (*a*) To how many pounds of 50° Bé. sulphuric acid are 350 cubic feet of 52° Bé. sulphuric acid equivalent? (*b*) If 60° Bé. sulphuric acid contains 77.67% H_2SO_4, to how many pounds of 60° Bé. sulphuric acid are 530 cubic feet of 52° Bé. acid equivalent?

Ans. (*a*) 35,647.5 lbs.,
(*b*) 43,216.2 lbs.

506. Calculate the equivalent weight in terms of 60° Bé. sulphuric acid equivalent to 2310 cubic feet, measured at 102 F., a sample of which showed 59.66° Bé. at 80° F.

Ans. 243,150 lbs.

507. Calculate the weight of 50° Bé. sulphuric acid equivalent to a shipment of 2160.61 cubic feet, measured at 120° F., a sample of which showed 56.14° Bé. at 80° F.[1]

Ans. 252,410 lbs.

508. How many pounds of 60° Bé. sulphuric acid are equivalent to a shipment of 2507 cubic feet measured at 92° F., a sample of which showed 65.52° Bé. at 77° F.?

Ans. 282,614 lbs.

509. It is required to make 37,000 lbs. of a mixed acid of the composition:

	Per cent
H_2SO_4	41.00
HNO_3	52.00
H_2O	7.00

there remaining in the mixing tank 6720 lbs. of an acid from a former mix of the composition:

[1] In commercial transactions, calculations are often carried to a degree of accuracy unwarranted by the accuracy of the readings.

	Per cent
H_2SO_4	42.00
HNO_3	52.54
H_2O	5.46

How many pounds of 98.00% sulphuric acid, and 94.70% and 61.40% of nitric acid must be added to the acid already in the tank to make this mix? *Ans.* 12,599.6 lbs. 98.00% H_2SO_4,
14,574.3 lbs. 94.70% HNO_3,
3,106.1 lbs. 61.40% HNO_3.

510. If nitric acid to the extent of one per cent is lost in mixing the acids by reason of heat generated or other reasons, calculate the quantities called for in Problem 509 so that after mixing the acid will have the desired composition.

Ans. 12,600 lbs. 98.00% H_2SO_4,
15,689 lbs. 94.70% HNO_3,
1,991 lbs. 61.40% HNO_3.

511. Calculate the amounts of acid required to make 34,000 lbs. of a mixed acid of the composition:

	Per cent
H_2SO_4	65.00
HNO_3	18.10
H_2O	16.90

there remaining in the tank 3780 lbs. of an acid from a former mix, the composition of which is

	Per cent
H_2SO_4	42.00
HNO_3	52.00
H_2O	6.00

it being also desired to use in making this mix, in order to work it off, 7000 lbs. of an acid of

	Per cent
H_2SO_4	64.00
HNO_3	25.00
H_2O	11.00

The sulphuric acid is to be added as 93.20% H_2SO_4, and the nitric acid as 52.30% HNO_3; water, if any be required, is to be added

as such. How many pounds of these substances must be taken, in addition to the acid already in the tank and the 7000 lbs. of the acid which it is desired to work off?

Ans. 17,531 lbs. 93.2% H_2SO_4,
4,260 lbs. 52.3% HNO_3,
1,429 lbs. water.

512. Calculate how much 93.20% H_2SO_4, the acid to be worked off, and water must be added in problem (511) that a maximum amount of the acid to be worked off may be used, adding no 52.30% HNO_3.

Ans. 14,957 lbs. acid to be worked off,
12,067 lbs. 93.2% H_2SO_4,
3,196 lbs. water.

513. How many pounds of 98.00% sulphuric acid, and 96.00% and 61.4% nitric acid must be taken to make 60,000 lbs. of a mixed acid of the composition:

	Per cent
H_2SO_4	46.00
HNO_3	48.00
H_2O	6.00

Ans. 28,163 lbs. 98.0% H_2SO_4,
26,711 lbs. 96.0% HNO_3,
5,126 lbs. 61.4% HNO_3.

514. It is required to make a mixed acid of the composition:

	Per cent
H_2SO_4	46.00
HNO_3	49.00
H_2O	5.00

from 96.00% and 61.4% nitric acid and 98.00% sulphuric acid. How many pounds of each must be taken to prepare 60,000 lbs.?

Ans. 28,163 lbs. 98.0% H_2SO_4,
28,474 lbs. 96.0% HNO_3,
3,363 lbs. 61.4% HNO_3.

515. How many pounds of 95.00% nitric acid and 30.00% oleum must be added for each 1000 lbs. of a mixed acid of the composition:

	Per cent
H_2SO_4	43.00
HNO_3	51.00
H_2O	6.00

to convert into a mixed acid of the composition:

	Per cent
H_2SO_4	42.00
HNO_3	53.00
H_2O	5.00

Ans. 137.07 lbs. 95% HNO_3,
71.38 lbs. 30% oleum.

516. It is required to make 61,320 lbs. of a mixed acid of the composition:

	Per cent
HNO_3	56.00
H_2SO_4	41.00
H_2O	3.00

there remaining in the tank, from a former mix, 2604 lbs. of an acid of the composition:

	Per cent
HNO_3	52.00
H_2SO_4	42.50
H_2O	5.50

How many pounds of a 20.00% oleum, 98.56% sulphuric acid and 94.50 nitric acid must be added to the acid already in the tank? *Ans.* 9,678 lbs. 20.00% oleum,
14,133 lbs. 98.56% H_2SO_4,
34,905 lbs. 94.50% HNO_3.

APPENDIX

XXXV. — SUL

By W. C. Ferguson

Degrees Baumé.	Specific Gravity $\frac{60°}{60°}$F.	Degrees Twaddell.	Per cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per cent O. V.*	Pounds O. V. in 1 Cubic Foot.
0	1.0000	0.0	0.00	62.37	0.00	0.00
1	1.0069	1.4	1.02	62.80	1.09	0.68
2	1.0140	2.8	2.08	63.24	2.23	1.41
3	1.0211	4.2	3.13	63.69	3.36	2.14
4	1.0284	5.7	4.21	64.14	4.52	2.90
5	1.0357	7.1	5.28	64.60	5.67	3.66
6	1.0432	8.6	6.37	65.06	6.84	4.45
7	1.0507	10.1	7.45	65.53	7.99	5.24
8	1.0584	11.7	8.55	66.01	9.17	6.06
9	1.0662	13.2	9.66	66.50	10.37	6.89
10	1.0741	14.8	10.77	66.99	11.56	7.74
11	1.0821	16.4	11.89	67.49	12.76	8.61
12	1.0902	18.0	13.01	68.00	13.96	9.49
13	1.0985	19.7	14.13	68.51	15.16	10.39
14	1.1069	21.4	15.25	69.04	16.36	11.30
15	1.1154	23.1	16.38	69.57	17.58	12.23
16	1.1240	24.8	17.53	70.10	18.81	13.19
17	1.1328	26.6	18.71	70.65	20.08	14.18
18	1.1417	28.3	19.89	71.21	21.34	15.20
19	1.1508	30.2	21.07	71.78	22.61	16.23
20	1.1600	32.0	22.25	72.35	23.87	17.27
21	1.1694	33.9	23.43	72.94	25.14	18.34
22	1.1789	35.8	24.61	73.53	26.41	19.42
23	1.1885	37.7	25.81	74.13	27.69	20.53
24	1.1983	39.7	27.03	74.74	29.00	21.68

Sp. Gr. determinations were made at 60° F., compared with water at 60° F.

From the Sp. Grs., the corresponding degrees Baumé were calculated by the following formula: Baumé = 145 − 145/Sp. Gr.

Baumé Hydrometers for use with this table must be graduated by the above formula, which formula should always be printed on the scale.

* 66° Baumé = Sp. Gr. 1.8354 = Oil of Vitriol (O. V.).

1 cu. ft. water at 60° F. weighs 62.37 lbs. av.

Atomic weights from F. W. Clarke's table of 1901. O = 16.

H_2SO_4 = 100 per cent.

	% H_2SO_4	% O. V.	% 60°
O. V. =	93.19	100.00	119.98
60° =	77.67	83.35	100.00
50° =	62.18	66.72	80.06

PHURIC ACID

AND H. P. TALBOT

Degrees Baumé.	* Freezing (Melting) Point. F.
0	32.0
1	31.2
2	30.5
3	29.8
4	28.9
5	28.1
6	27.2
7	26.3
8	25.1
9	24.0
10	22.8
11	21.5
12	20.0
13	18.3
14	16.6
15	14.7
16	12.6
17	10.2
18	7.7
19	4.8
20	+ 1.6
21	− 1.8
22	− 6.0
23	−11
24	−16

APPROXIMATE BOILING POINTS

50° B, 295° F.
60° " 386° "
61° " 400° "
62° " 415° "
63° " 432° "
64° " 451° "
65° " 485° "
66° " 538° "

FIXED POINTS

Specific Gravity.	Per Cent H_2SO_4.	Specific Gravity.	Per Cent H_2SO_4.
1.0000	.00	1.5281	62.34
1.0048	.71	1.5440	63.79
1.0347	5.14	1.5748	66.51
1.0649	9.48	1.6272	71.00
1.0992	14.22	1.6679	74.46
1.1353	19.04	1.7044	77.54
1.1736	23.94	1.7258	79.40
1.2105	28.55	1.7472	81.32
1.2513	33.49	1.7700	83.47
1.2951	38.64	1.7959	86.36
1.3441	44.15	1.8117	88.53
1.3947	49.52	1.8194	89.75
1.4307	53.17	1.8275	91.32
1.4667	56.68	1.8354	93.19
1.4822	58.14	.....	.....

Acids stronger than 66° Bé. should have their percentage compositions determined by chemical analysis.

* Calculated from Pickering's results, Jour. of Lon. Ch. Soc., vol. 57, p. 363.

AUTHORITIES — W. C. FERGUSON; H. P. TALBOT.

This table has been approved and adopted as a standard by the Manufacturing Chemists' Association of the United States.

W. H. BOWER,
HENRY HOWARD,
JAS. L. MORGAN,
ARTHUR WYMAN,
A. G. ROSENGARTEN,
Executive Committee.

New York, June 23, 1904.

Degrees Baumé.	Specific Gravity $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cubic Foot.
25	1.2083	41.7	28.28	75.36	30.34	22.87
26	1.2185	43.7	29.53	76.00	31.69	24.08
27	1.2288	45.8	30.79	76.64	33.04	25.32
28	1.2393	47.9	32.05	77.30	34.39	26.58
29	1.2500	50.0	33.33	77.96	35.76	27.88
30	1.2609	52.2	34.63	78.64	37.16	29.22
31	1.2719	54.4	35.93	79.33	38.55	30.58
32	1.2832	56.6	37.26	80.03	39.98	32.00
33	1.2946	58.9	38.58	80.74	41.40	33.42
34	1.3063	61.3	39.92	81.47	42.83	34.90
35	1.3182	63.6	41.27	82.22	44.28	36.41
36	1.3303	66.1	42.63	82.97	45.74	37.95
37	1.3426	68.5	43.99	83.74	47.20	39.53
38	1.3551	71.0	45.35	84.52	48.66	41.13
39	1.3679	73.6	46.72	85.32	50.13	42.77
40	1.3810	76.2	48.10	86.13	51.61	44.45
41	1.3942	78.8	49.47	86.96	53.08	46.16
42	1.4078	81.6	50.87	87.80	54.58	47.92
43	1.4216	84.3	52.26	88.67	56.07	49.72
44	1.4356	87.1	53.66	89.54	57.58	51.56
45	1.4500	90.0	55.07	90.44	59.09	53.44
46	1.4646	92.9	56.48	91.35	60.60	55.36
47	1.4796	95.9	57.90	92.28	62.13	57.33
48	1.4948	99.0	59.32	93.23	63.65	59.34
49	1.5104	102.1	60.75	94.20	65.18	61.40
50	1.5263	105.3	62.18	95.20	66.72	63.52
51	1.5426	108.5	63.66	96.21	68.31	65.72
52	1.5591	111.8	65.13	97.24	69.89	67.96
53	1.5761	115.2	66.63	98.30	71.50	70.28
54	1.5934	118.7	68.13	99.38	73.11	72.66
55	1.6111	122.2	69.65	100.48	74.74	75.10
56	1.6292	125.8	71.17	101.61	76.37	77.60
57	1.6477	129.5	72.75	102.77	78.07	80.23
58	1.6667	133.3	74.36	103.95	79.79	82.95
59	1.6860	137.2	75.99	105.16	81.54	85.75

Degrees Baumé.	* Freezing (Melting) Point. °F.	ALLOWANCE FOR TEMPERATURE
25	−23	At 10° Bé. .029° Bé. or .00023 Sp. Gr. = 1° F.
26	−30	" 20° " .036° " .00034 " = 1° "
27	−39	" 30° " .035° " .00039 " = 1° "
28	−49	" 40° " .031° " .00041 " = 1° "
29	−61	" 50° " .028° " .00045 " = 1° "
		" 60° " .026° " .00053 " = 1° "
30	−74	" 63° " .026° " .00057 " = 1° "
31	−82	" 66° " .0235° " .00054 " = 1° "
32	−96	
33	−97	
34	−91	

Degrees Baumé.	* Freezing (Melting) Point. °F.	Per Cent 60° Baumé.	Pounds 60° Baumé in 1 Cubic Foot.	Per Cent 50° Baumé.	Pounds 50° Baumé in 1 Cubic Foot.
35	−81				
36	−70				
37	−60				
38	−53				
39	−47				
40	−41	61.93	53.34	77.36	66.63
41	−35	63.69	55.39	79.56	69.19
42	−31	65.50	57.50	81.81	71.83
43	−27	67.28	59.66	84.05	74.53
44	−23	69.09	61.86	86.30	77.27
45	−20	70.90	64.12	88.56	80.10
46	−14	72.72	66.43	90.83	82.98
47	−15	74.55	68.79	93.12	85.93
48	−18	76.37	71.20	95.40	88.94
49	−22	78.22	73.68	97.70	92.03
50	−27	80.06	76.21	100.00	95.20
51	−33	81.96	78.85	102.38	98.50
52	−39	83.86	81.54	104.74	101.85
53	−49	85.79	84.33	107.15	105.33
54	−59	87.72	87.17	109.57	108.89
55	..	89.67	90.10	112.01	112.55
56	..	91.63	93.11	114.46	116.30
57	..	93.67	96.26	117.00	120.24
58	..	95.74	99.52	119.59	124.31
59	− 7	97.84	102.89	122.21	128.52

Below 40

Degrees Baumé.	Specific Gravity $\frac{60°}{60°}$ F.	Degrees Twaddell.	Per Cent H_2SO_4.	Weight of 1 Cu. Ft. in Lbs. Av.	Per Cent O. V.	Pounds O. V. in 1 Cubic Foot.
60	1.7059	141.2	77.67	106.40	83.35	88.68
61	1.7262	145.2	79.43	107.66	85.23	91.76
62	1.7470	149.4	81.30	108.96	87.24	95.06
63	1.7683	153.7	83.34	110.29	89.43	98.63
64	1.7901	158.0	85.66	111.65	91.92	102.63
64¼	1.7957	159.1	86.33	112.00	92.64	103.75
64½	1.8012	160.2	87.04	112.34	93.40	104.93
64¾	1.8068	161.4	87.81	112.69	94.23	106.19
65	1.8125	162.5	88.65	113.05	95.13	107.54
65¼	1.8182	163.6	89.55	113.40	96.10	108.97
65½	1.8239	164.8	90.60	113.76	97.22	110.60
65¾	1.8297	165.9	91.80	114.12	98.51	112.42
66	1.8354	167.1	93.19	114.47	100.00	114.47

XXXVI. — FUMING SULPHURIC ACID AT 20°

CL. WINKLER

Specific Gravity.	Total SO_3.	100 Parts Contain			Specific Gravity.	Total SO_3.	100 Parts Contain		
		Free SO_3.*	H_2SO_4.	Acid of 66° B.			Free SO_3.*	H_2SO_4.	Acid of 66° B.
1.835	75.31	...	92.25	99	1.905	83.57	10.56	89.44	65.68
1.840	77.38	...	94.79	90.69	1.910	83.73	11.43	88.57	65.25
1.845	79.28	...	97.11	83.08	1.915	84.08	13.33	86.67	63.84
1.850	80.01	...	98.01	80.10	1.920	84.56	15.95	84.05	62.10
1.855	80.95	...	99.16	76.38	1.925	85.06	18.67	81.33	59.90
1.860	81.84	1.54	98.46	72.81	1.930	85.57	21.34	78.66	57.86
1.865	82.12	2.66	97.34	71.71	1.935	86.23	25.65	74.35	55.21
1.870	82.41	4.28	95.76	70.53	1.940	86.78	28.03	71.97	53.00
1.875	82.63	5.44	94.56	69.35	1.945	87.13	29.94	70.06	51.60
1.880	82.81	6.42	93.58	68.92	1.950	87.41	31.46	63.54	50.48
1.885	82.97	7.29	92.71	68.27	1.955	87.65	32.77	67.23	49.52
1.890	83.13	8.16	91.94	67.55	1.960	88.22	35.87	64.13	47.23
1.895	83.43	9.34	90.66	66.81	1.965	88.92	39.68	60.32	44.42
1.900	83.48	10.07	89.93	66.24	1.970	89.83	44.64	55.36	40.78

* This column gives the amount of SO_3 which may be distilled off.

Degrees Baumé.	* Freezing (Melting) Point.	Per Cent 60° Baumé.	Pounds 60° Baumé in Cubic Foot.	Per Cent 50° Baumé.	Pounds 50° Baumé in Cubic Foot.
60	+12.6	100.00	106.40	124.91	132.91
61	27.3	102.27	110.10	127.74	137.52
62	39.1	104.67	114.05	130.75	142.47
63	46.1	107.30	118.34	134.03	147.82
64	46.4	110.29	123.14	137.76	153.81
64¼	43.6	111.15	124.49	138.84	155.50
64½	41.1	112.06	125.89	139.98	157.25
64¾	37.9	113.05	127.40	141.22	159.14
65	33.1	114.14	129.03	142.57	161.17
65¼	24.6	115.30	130.75	144.02	163.32
65½	13.4	116.65	132.70	145.71	165.76
65¾	−1	118.19	134.88	147.63	168.48
66	−29	119.98	137.34	149.87	171.56

XXXVII. — SULPHURIC ACID

94–100% H_2SO_4

By H. B. Bishop

The acid used in this table was prepared from Baker and Adamson's c.p. sulphuric acid 95 per cent, which was strengthened to 100 per cent by the addition of fuming sulphuric acid made by distilling fuming acid (70 per cent free SO_3) into a portion of the 95 per cent c.p. acid. The final acid was tested for impurities: residue upon evaporation, chlorine, niter and sulphur dioxide. The only impurity found was a trace of sulphur dioxide (0.001 per cent) which was less than the sensitiveness of the determination.

The analytical and specific gravity determinations, and the allowance for temperature were made in the same manner, and with the same accuracy as in the sulphuric acid table adopted in 1904, the specific gravity 1.8354 and 93.19 per cent H_2SO_4 being taken as a standard.

The actual determinations were made within a few hundredths of a per cent of the points given in the table, the even percentages being calculated by interpolation.

Per Cent H_2SO_4.	Sp. Gr. at 60° F.	Allowance for Temperature.
66° Bé. 93.19	1.8354	At 94% 0.00054 sp. gr. = 1° F.
94.00	1.8381	At 96% 0.00053 sp. gr. = 1° F.
95.00	1.8407	At 97.5% 0.00052 sp. gr. = 1° F.
96.00	1.8427	At 100% 0.00052 sp. gr. = 1° F.
97.00	1.8437	
97.50	1.8439	
98.00	1.8437	
99.00	1.8424	
100.00	1.8391	

TENSION OF AQUEOUS VAPOR

Temp. °C.	Press., mm.	Temp. °C.	Press., mm.	Temp. °C.	Press., mm.
0°	4.60	12°	10.48	24°	22.18
1°	4.92	13°	11.19	25°	23.55
2°	5.29	14°	11.94	26°	24.99
3°.	5.68	15°	12.73	27°	26.50
4°	6.09	16°	13.57	28°	28.10
5°	6.53	17°	14.45	29°	29.78
6°	7.00	18°	15.38	30°	31.56
7°	7.49	19°	16.37	31°	33.42
8°	8.02	20°	17.41	32°	35.37
9°	8.58	21°	18.50	33°	37.43
10°	9.18	22°	19.66	34°	39.59
11°	9.81	23°	20.88	35°	41.85

Mensuration

$\pi = 3.1416$.

Length of circle (radius r) $= 2\pi r$.

Area of triangle (base b, altitude a) $= \frac{ab}{2}$.

Area of circle (radius r) $= \pi r^2$.

Surface of sphere (radius r) $= 4\pi r^2$.

Surface of cylinder (radius r, height h) $= 2\pi r\,(r + h)$.

Surface of cone (radius r, slant height l) $= \pi r\,(r + l)$.

Volume of sphere (radius r) $= \frac{4}{3}\pi r^3$.

Volume of cylinder (radius r, height h) $= \pi r^2 h$.

Gases

(WEIGHT AT STANDARD CONDITIONS, 0° C. AND 760 MM.)

Air	1.2926 grams
Carbon dioxide	1.9768 grams
Hydrogen	0.089873 grams
Nitrogen	1.2507 grams
Oxygen	1.4292 grams

Miscellaneous

One pound avoirdupois = 453.59 grams.
One meter = 39.37 inches.
One gallon = 231 cubic inches.
One cubic foot of water at 60° F. weighs 62.37 pounds.

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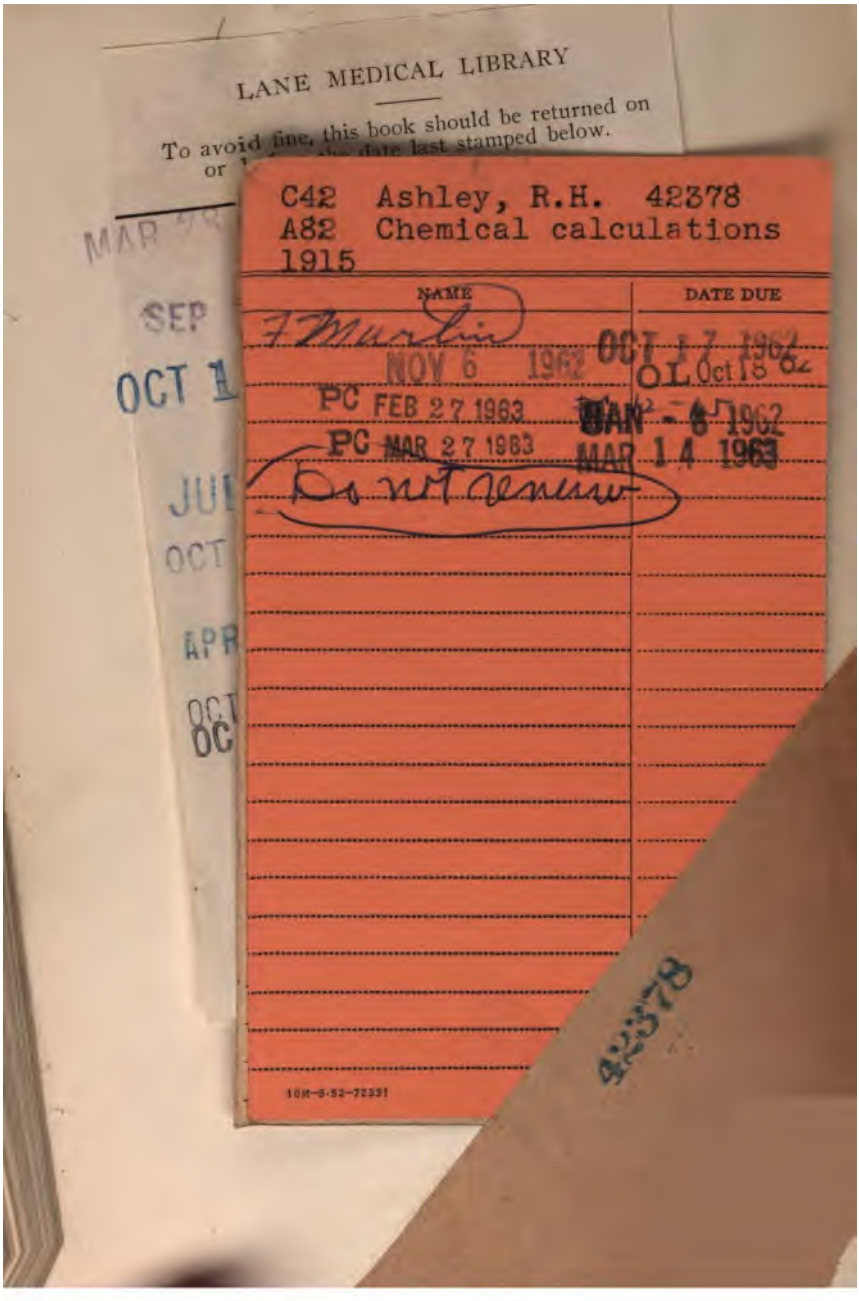
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Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.00	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.6
Chlorine	Cl	35.46	Radium	Ra	226.4
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.07
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.10	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	172.0
Lutecium	Lu	174.0	Yttrium	Yt	89.0
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

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